

III. *On the Measurement of Temperature. Part I.—On the Pressure Coefficients of Hydrogen and Helium at Constant Volume and at different Initial Pressures. Part II.—On the Vapour Pressures of Liquid Oxygen at Temperatures below its Boiling-Point on the Constant-Volume Hydrogen and Helium Scales. Part III.—On the Vapour Pressures of Liquid Hydrogen at Temperatures below its Boiling-Point on the Constant-Volume Hydrogen and Helium Scales.*

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[PLATE 1.]

PART I.

*On the Pressure Coefficients of Hydrogen and Helium at Constant Volume and at different Initial Pressures.*

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### 1. *Introduction.*

CONSIDERING how much depends upon our knowledge of the relationship between the thermodynamic scale of temperature and the various scales of temperature as determined by means of gas thermometers, it is surprising that so little attention has been paid to the matter in recent years. Indeed, instead of attempting to arrive at the necessary experimental data for the solution of the problem, it appears as if chemists and physicists were prepared to accept arbitrary scales of temperature, which differ considerably one from another.

Since the problem was first attacked by JOULE and Lord KELVIN, more than half a century ago, it has been made the subject of investigation by more than one mathematician. Recently ('Phil. Mag.,' 1901, vol. 2, p. 130) J. ROSE-INNES has succeeded in developing some fairly simple equations by means of which the difference between the thermo-dynamic scale of temperature and the temperature determined by means of gas thermometers can be calculated. The data necessary in the case of each gas are the following:—

- (a.) The coefficient of increase of pressure at constant volume.
- (b.) The coefficient of increase of volume at constant pressure.
- (c.) The variation of "p.v." with pressure at different temperature.
- (d.) The Joule-Thomson effect and its variation with temperature.

Applying existing data to his equations, ROSE-INNES arrived at results which, as the following table shows, are anything but satisfactory:—

Correction of the Constant-Volume Thermometer.

Gas.	Pressure on gas at ice-point.	Temperature of ice- point (reciprocal of pressure coefficient).	Correction.	Absolute ice- point.
Hydrogen . . . . .	millims. 1000	273·04	0·12	273·16
Nitrogen . . . . .	995	272·13	1·23	273·36

## Correction of the Constant-Pressure Thermometer.

Gas.	Temperature of ice-point (reciprocal of volume coefficient).	Correction.	Absolute ice-point.
Hydrogen . . . . .	273·13	-0·13	273·00
Nitrogen . . . . .	273·44	0·72	273·16

Of the data employed in making the foregoing calculation only the pressure coefficients of hydrogen and nitrogen, which have been determined by P. CHAPPUIS, of the "Bureau International des Poids et Mesures," and the variation of "p.v." with pressure at the normal temperature, which has been recently investigated by ONNES ('Leiden Laboratory Reports,' 1901) in the case of hydrogen, can be considered as being known with sufficient certainty. AMAGAT has determined the variations of "p.v." for nitrogen, but the experiment was made at high pressure and not at the pressure under which thermometric measurements are usually made. In view of the fact that both air and oxygen appear to obey BOYLE'S law at pressures below 150 millims. of mercury (RAYLEIGH, 'Phil. Trans.,' A, vol. 198, p. 417), extrapolation of AMAGAT'S results at high pressure does not seem justifiable; and to obtain the data necessary for the correction of the gas thermometer the variations of "p.v." should be carefully investigated at pressures below two atmospheres. REGNAULT'S values for the volume coefficients of nitrogen and hydrogen are not to be relied upon.

The Joule-Thomson effect for air and hydrogen was determined by JOULE and Lord KELVIN more than half a century ago. Without discussing their results, it may be pointed out that by employing electrical methods for the measurement of temperature, it should now be possible to measure the effect with a much higher degree of accuracy, and over a wider range of temperature than was then possible. An investigation in this direction has been commenced by Dr. R. A. LEHFELDT conjointly with one of us.

## 2. *Suitable Thermometric Substances.*

For the reason that the composition of atmospheric air varies with the prevailing condition, air is not a suitable substance for use in thermometry. Atmospheric nitrogen appears, however, to contain a constant quantity of argon and its companions, and may be employed in thermometry over a range, limited, perhaps, by the temperatures at which it condenses on the one hand and dissociates on the other.

Until recently, hydrogen appeared to be the most important thermometric substance.

The constant-volume hydrogen scale appeared to approximate closely to the absolute scale of temperature, and the gas could be employed in any measurements to which thermometers could be applied. For this reason the Comité International adopted as the normal scale of temperature the scale of a constant-volume hydrogen thermometer, in which the pressure at the ice-point was 1000 millims. of mercury.

Recently, however, we have succeeded in reaching temperatures at which the vapour pressure of hydrogen itself is extremely small, and which cannot be investigated by means of the hydrogen thermometer with any degree of accuracy (see p. 179). Further, it has now been ascertained that at high temperatures hydrogen will reduce glass, porcelain, and even silica; and as the gas diffuses readily through the walls of platinum vessels, its application in this direction must be considered limited.

It has been pointed out by one of us ("Experimental Study of Gases," p. 156) that pure helium appears to be a much more perfect thermometric substance than hydrogen. It is chemically inactive; and, so far as we can predict, is incapable of undergoing dissociation at high temperatures. Hence it is probable that measurements of high temperatures, made by means of quartz thermometers filled with helium, are alone to be relied upon. For the measurement of low temperatures it presents similar advantages; for as it appears probable that its critical point lies below  $12^{\circ}$  abs., it may be considered as remaining a very perfect gas down to the lowest temperatures which it has hitherto been possible to reach.

Further, as the following results show, the hydrogen and helium scales agree closely between  $0^{\circ}$  and  $100^{\circ}$  C., and consequently it may be assumed that at temperatures above  $0^{\circ}$  C. the difference between the thermo-dynamic scale of temperature and the scale of a constant-volume thermometer filled with one of these gases is small. At lower temperatures the divergence between the two scales is small, but the contraction of the helium being always less than that of the hydrogen indicates that the former remains the more perfect gas. Unless some hitherto unknown objection is attached to the use of the helium thermometer, the helium scale should replace the hydrogen scale as the normal scale of temperature.

### *3. Previous Measurements of the Pressure Coefficient of Hydrogen and Helium.*

The first step in the series of researches on which we have embarked consisted in the determination of the pressure coefficients at constant volume of hydrogen and helium between the melting-point of ice and the boiling-point of water under standard pressure, which, in the basement of University College, is equivalent to 759.56 millims. of mercury at  $0^{\circ}$  C. The coefficient for hydrogen, at a pressure of 100 millims. of mercury at the ice-point, is given by CHAPPUIS ("Travaux et Mémoires du Bureau International des Poids et Mesures") as 0.00366254, the mean of seven determinations, of which the highest is 0.00366271 and the lowest 0.00366231, and on this deter-



mination the normal scale of temperature of the Comité International is based. Kammerlingh ONNES ('Leiden Communications,' 1901, No. 60) gives 0.0036627 as the value of the coefficient, the actual numbers being 0.0036624, 0.0036628, 0.0036628. The result obtained by REGNAULT, 0.0036613, need not now be considered.

It has hitherto been assumed that the pressure coefficient for hydrogen is independent of the initial pressure, and does not, as in the case of nitrogen, decrease and at length attain a limiting value. As important deductions have been based on this statement, we decided to measure the coefficient for our standard gases at initial pressures corresponding to 350, 500, and 700 millims. of mercury.

An approximate measurement of the pressure coefficient of helium was made by KUENEN and RANDALL in 1895 ('Phil. Mag.'). In employing the helium thermometer for the measurement of low temperatures, OLSZEWSKI assumed that the coefficient is the same as that of hydrogen.

#### 4. Accuracy of the Results.

In order to determine the fifth significant figure in the pressure coefficient, the total error must not exceed 1 part in 40,000, a degree of accuracy which it is practically impossible to attain in individual experiments. As will be seen later, the greatest error in our observations may be attributed to inaccuracy in the scale which, over the whole length, may be considered accurate to at least 0.01 millim., or to  $1/25,000$  of the increase of pressure on the gas between  $0^{\circ}$  and  $100^{\circ}$  C. at an initial pressure of 700 millims.

#### 5. Apparatus employed in the Research. The Barometer.

Since at the boiling-point of water a change of pressure of 0.1 millim. of mercury corresponds to a change of temperature of  $0.0036^{\circ}$  C., or  $1/20,000$  of the difference between the boiling and freezing-points of water, it was sufficient to observe the atmospheric pressure with this degree of accuracy. The barometer employed is shown in fig. 1; it was constructed by us specially for this research. The upper chamber A was 20 millims. in diameter and 200 millims. in length. It was sealed to the stem B, which was drawn out at the lower end C to a capillary tube of an internal diameter of about 1 millim. In filling the barometer, the capillary end of the tube B was sealed to a T tube (fig. 2), of which the branch D led to the mercury pump, and the branch C projected

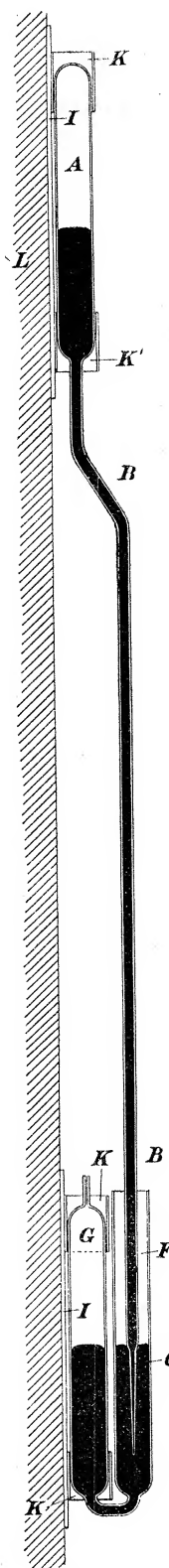


Fig. 1.

downward and was drawn to a fine point, which was sealed. The portions A and B of the apparatus were heated, and, when the apparatus was thoroughly exhausted, the point of the tube E was broken below the surface of some warm mercury in a basin. The mercury entered slowly, and, passing through the constriction C, ran

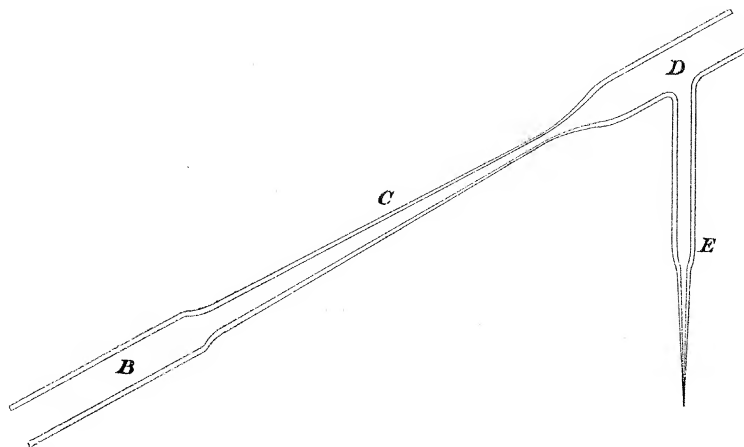


Fig. 2.

down into A, which was heated sufficiently to boil the liquid. When the apparatus was completely filled, the tube was cut through the constriction C, and the small bubble of air which remained in B was replaced by mercury.

Both the upper chamber and the limb of the U tube which formed the lower chamber were set by means of plaster of Paris into brass mounts KK', which were soldered to plates II', shown in section in the drawing. In the case of the upper chamber this was done after it had been filled with mercury. In setting up the barometer the U tube FG was first fixed to the piece of wood L which supported the instrument, and was then filled with mercury. The upper portion was then inverted, the open end plunged into the limb F of the U tube, and the brass plate I screwed to wooden support L. A dish was placed below the apparatus to catch the mercury overflowing from F; finally some of the mercury in the U tube was removed by means of a syphon, so that the surface of the mercury in the upper and lower chambers appeared as in the figure.

The scale, which was placed in front of the barometer, consisted of a piece of plate-glass to which were joined, by means of Canada balsam, two short scales 100 millims. in length and divided in millimetres. To prevent them shifting, through the flowing of the cement, they were further fixed by a binding of copper-wire covered with plaster of Paris at the top and bottom. The scale was compared with a standard scale from the Physikalische Reichsanstalt at Charlottenburg, and afterwards at the National Physical Laboratory with a standard metre (p. 119). The temperature of the column of mercury was measured by means of a thermometer divided to  $\frac{1}{20}^{\circ}$  C. placed half-way between the top and bottom.

Readings of the barometer were made by means of two telescopes placed on a stand opposite the instrument. The barometer itself was attached to a pillar so that a card placed behind (fig. 3) it at an angle of  $45^\circ$  to the line of sight gave a good illumination from a window at the side. The upper half of the card was black, the lower half white, and before taking a reading the card was adjusted so that the dividing line appeared about 1 millim. above the surface of the mercury. By this arrangement the meniscus appeared perfectly sharp, as all surface reflections were completely eliminated.

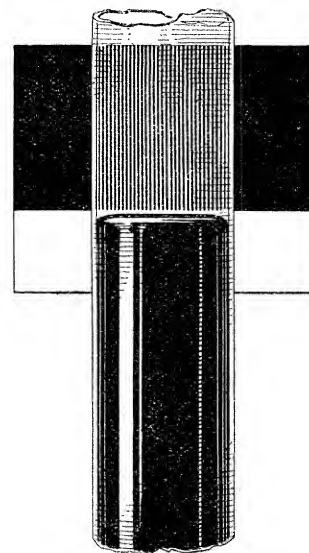


Fig. 3.

*Mercury Thermometers.*—The mercury thermometers employed in these observations were compared with the thermometer employed to measure the temperature of the dead-space. This thermometer was itself compared with the gas thermometer and the error over the small range of temperature required, viz.,  $8^\circ$  to  $12^\circ$  C., was known to within  $0.02^\circ$ . The weight of such an error will be discussed later.

#### 6. *The Constant-Volume Thermometer.*

The apparatus employed in the determination of the pressure coefficients of the gases differs in many respects from that employed by other observers. CHAPPUIS employed thermometers of hard glass and of platino-iridium, and ONNES bulbs of hard glass; in both cases the connection between the thermometer bulb and the dead-space was made by means of a steel tube connected with the glass by means of cement.

Beyond the fact that hard glass has a slightly lower coefficient of expansion than soda glass, there is no advantage in employing it; on the other hand, soda glass is more easily worked, and as by using it the bulb, stem, and dead-space can all be made in one piece, considerable advantage is to be gained. The bulb of our instrument (fig. 4) was made by sealing a piece of glass tube 30 millims. in diameter to a capillary tube 0.75 millim. in internal diameter, which for convenience in calibration was divided in millimetres for a portion of its length. The stem was bent at right angles at C (fig. 4), and ultimately sealed at D to the portion of the stem leading to the dead-space.

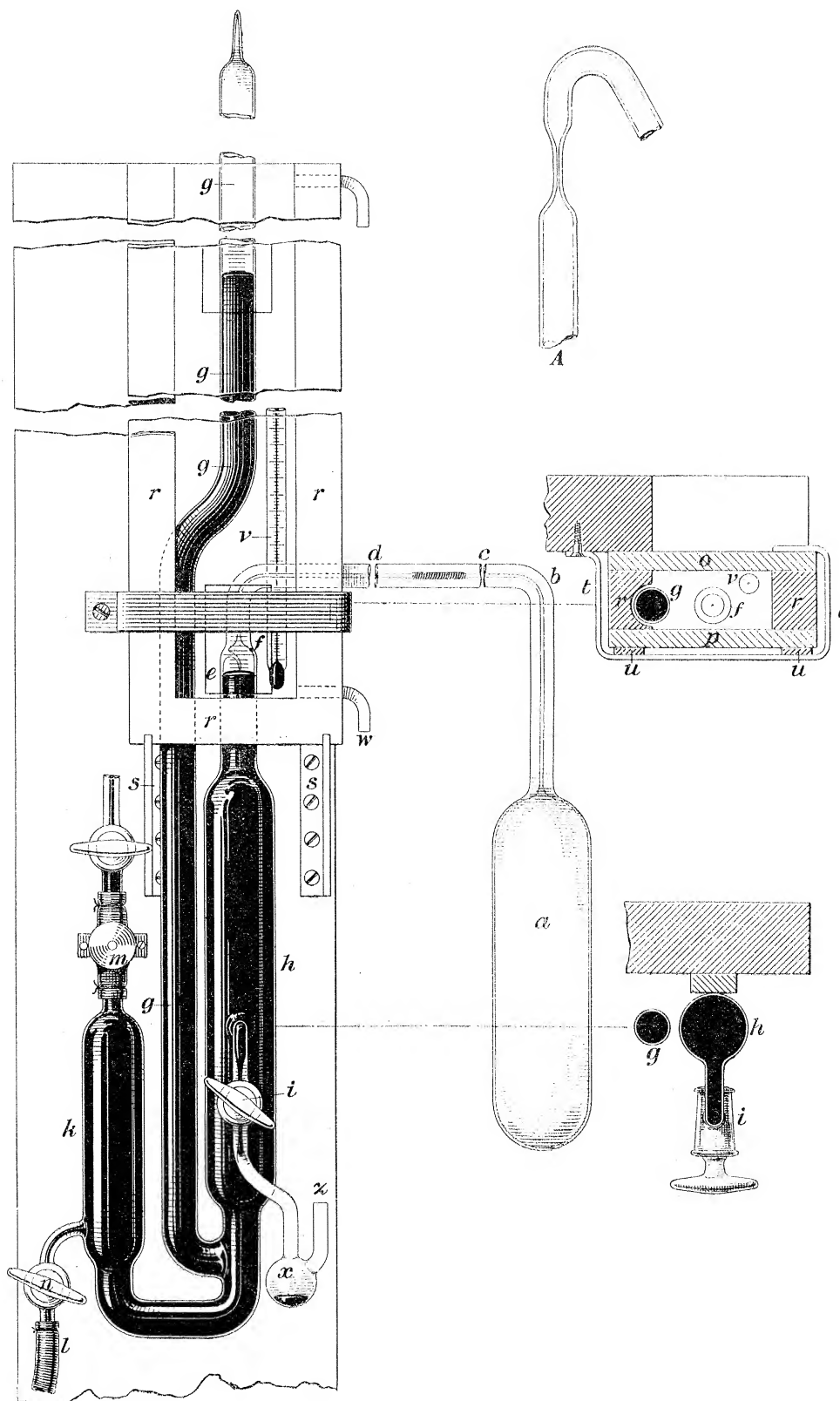


Fig. 4.

7. *The Calibration of the Bulb.*

The volume of the bulb was determined by weighing it empty, and afterwards filled with water at the melting-point of ice. A glass tube was connected with the stem by a piece of rubber tube to prevent loss of water when the temperature rose. The following are the results :—

	(a.)	(b.)
Weight of bulb empty . . . . .	71·9551	71·9568
Weight of bulb filled with water at 0° C. to division 126 on stem . . . . .	170·6657	170·6657
Weight of catch water . . . . .	4·5856	4·5860
Weight of water . . . . .	94·1230	
Weight of bulb corrected for weight of air in bulb, &c. . . . .	94·1975	
Volume of bulb to division 70 at 0° C. . . . .	94·2096	

The coefficient of expansion of the glass of which the thermometer bulb was made was determined by the weight-thermometer method. The weight-thermometer was made from the same glass tube as the thermometer bulb. The value for the coefficient was found to be 0·0000285.

The composition of the glass employed, which was obtained from Messrs. C. E. MÜLLER & Co., of High Holborn, appears to be very constant; for the coefficients of expansion of samples of it determined by KUENEN and RANDALL (*loc. cit.*, p. 109) in 1896, and by one of us in 1901, have the same value as that last determined.

The change of volume of the bulb due to change of the pressure on the gas inside it was also measured. It was determined by filling the bulb with water to a point on the stem and measuring the change in the position of the meniscus when the pressure was reduced by means of a water pump. The change of volume amounted to 0·0017 cub. centim. per atmosphere.

8. *The Dead-Space.*

Both CHAPPUIS and ONNES employed a glass tube with a steel cap attached to it by cement, and enclosing a steel point for the adjustment of the mercury meniscus. In the construction of our instrument we have entirely dispensed with steel and cement connection, and have employed an opaque glass point *e* sealed into the tube *f*, which formed the dead-space at its point of junction with the stem. The tube for the dead-space was cut from a piece of glass tube of 9 millims. internal diameter, selected for its straightness and regularity of bore; the manometer tube *g* was cut from the same piece. In making the junction with the capillary tube great care was

taken to heat only about 3 millims. of the wider tube, so as not to disturb the regularity of its surface at the level at which the mercury meniscus was afterwards observed. The operation of sealing the glass point into the tube was not an easy one.

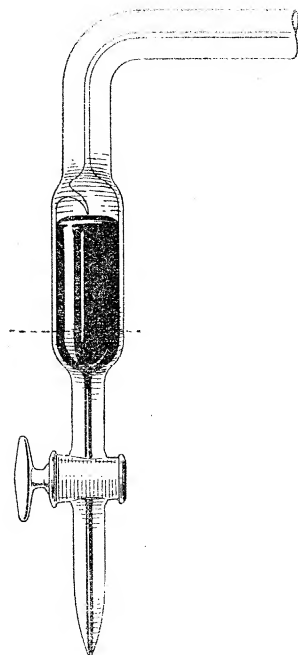


Fig. 5.

After bending the capillary tube as in the figure, the volume of the dead-space was determined in the following manner. The wide tube was cut about 30 millims. below its junction with the capillary tube and sealed to a capillary stop-cock drawn out to a point at its other end (fig. 5). The apparatus was fixed in a vertical position, a tap-funnel and rubber tube were attached to the stop-cock, and mercury was run into the tube till its surface came exactly into contact with the point; the final adjustment was made by closing the tap on the funnel and compressing the rubber tube with a screw-clip. The stop-cock on the dead-space was then closed, the rubber tube removed, and the mercury in the dead-space run out into a porcelain crucible and weighed. The rubber tube was then again attached to the apparatus, which was next filled with mercury to a mark on the stem. This mercury was weighed, and from the difference of the two weighings the volume of gas in the dead-space, between a

mercury meniscus in contact with the point and a mark on the stem, was calculated.

The experimental results are as follows :—

Weight of mercury from stop-cock to point.	Temperature.	Volume.
<i>a.</i> 34·1522	°C. 20·5	2·5213
<i>b.</i> 34·1684	20·1	2·5223
<i>c.</i> 34·1640	20·2	2·5220
		} 2·5219
Weight of mercury from stop-cock to mark on stem.		
<i>a.</i> 39·3633	} 20·0	2·9123
39·3638		
Volume of dead-space to mark on stem . . .		$\begin{array}{r} 2·9123 \\ 2·5219 \\ \hline 0·3904 \end{array}$

In making an actual experiment, the mercury in the dead-space was brought to within a short distance of the point; this distance was measured by means of the telescope and micrometer eye-piece used in measuring the pressure (p. 120). As the

volume of the dead-space was thus somewhat greater than that determined by the method just described, it was necessary to apply a correction amounting to  $\pi r^2 \Delta$ , where  $\Delta$  is the distance between the surface of the mercury and the point, and  $r$  is the radius of the tube (see p. 121);  $\pi r^2 = 0.636$ .

As will be shown later, it was necessary in measuring the pressure to apply a correction for the heights of the mercury meniscus in the dead-space and manometer tube of the thermometer, which varied slightly in every experiment. If the meniscus in the dead-space be considered to have the form of a semi-ellipsoid of height  $h$  and of radius  $r$ , the change of volume of the dead-space with change of height of the meniscus will be given by  $\frac{1}{3}\pi r^2(h - h')$ . The mean height of the meniscus was found to be 1.25 millims., and the extreme variation for any observation never exceeded 0.2 millim., which corresponds to a change of volume of 0.004 cub. centim. in the dead-space. As such an error had a considerable effect on the value of  $P_0$  and  $P_{100}$ , we were obliged to take it into consideration.

### 9. The Stem.

In our earlier experiment we had found that, if by any accident the mercury reached the top of the dead-space, minute globules of it adhered to the glass and were in time carried over into the bulb. As the vapour pressure of mercury is 0.27 millim. at 100° C., this gave rise to serious errors in our measurements.

To obviate this difficulty we introduced into a portion of the stem between  $c$  and  $d$  a closely-wound coil of silver wire 15 millims. long and slightly over 2 millims. in diameter. The tube was made slightly larger at this point. The volume of the air space was easily determined by weighing the tubes empty and full of water.

	(a.)	(b.)
Weight of stem filled with water . . . . .	10.4304	10.4306
„ „ empty . . . . .	10.3636	10.3632
„ water . . . . .	0.0668	0.0674
Volume of stem . . . . .	0.0671 cub. centim.	

### 10. Volumes of the Bulb, Stem, and Dead-Space.

When the instrument was set up permanently and the mercury brought close to the point in the dead-space, the whole of the internal space was considered as divided into three regions.

I. The bulb and stem to within 40 millims of the horizontal portion.

Volume at ice-point = 94.2096 cub. centims.

Volume at boiling-point =  $\left\{ 94.2096 (1 + 0.000285t) + 0.0017 \frac{P_{100} - P_0}{760} \right\}$  cub. centims.

II. The stem from the point already referred to to the middle of the wall of the water space enclosing the barometer tube. The temperature of the stem was determined with sufficient accuracy by means of a thermometer with the bulb placed between  $c$  and  $d$ .

$$\text{Volume} = 0.1031 \text{ cub. centim.}$$

In some of our earlier experiments, about 3 centims. of the stem outside the hypsometer was enclosed between sheets of asbestos, and the temperature was determined by means of a mercury thermometer. The mean temperature of this portion of the stem was usually about  $90^{\circ}\text{C}$ ., and, as its volume was only 0.0182 cub. centim., its temperature could be taken as  $100^{\circ}\text{C}$ . without affecting the value of  $P_{100}$ .

III. The dead-space and remainder of the stem. The dead-space and barometer were enclosed in a water jacket, as will be described presently; the temperature was determined by means of the thermometer  $v$ .

$$\text{Volume} = \{0.3904 + 0.636\Delta + 0.212(0.125 - h)\},$$

where  $\Delta$  is the distance in centimetres between the point and the surface of the mercury, and  $h$  is the height of the meniscus.

#### 11. *The Manometer and its Connection with the Dead-Space, &c.*

The pressure on the gas in the thermometer was determined directly by observing the difference of the level of this mercury meniscus in the dead-space  $f$  and in a manometer  $g$ . By employing this method it was necessary to take only two readings, and the observed pressures were entirely independent of the atmospheric pressure.

The tube  $f$  which formed the dead-space after removing the stop-cock was sealed at its lower end to a wider tube  $h$ , which was connected with the manometer tube  $g$  and with a tube  $k$ , which served to catch any air bubbles which might enter the apparatus through the stop-cock  $n$  and the rubber tube  $l$  leading to a mercury reservoir. A tube 5 millims. in diameter, sealed into the side of the tube  $h$ , was connected to a stop-cock  $i$  of capillary bore, through which the gas could be introduced into the apparatus. The tube  $k$  terminated above in a narrow glass tube, connected by a piece of india-rubber pressure tubing with one limb of a glass stop-cock, through which traces of air entering through the tube  $l$  could be expelled. By closing the stop-cock  $n$  and compressing the rubber tube by the pinch-cock  $m$  the final adjustment of the level of the mercury in the dead-space could be effected.

The manometer tube was carried vertically upwards from the bottom of  $h$  and bent above the level of the dead-space, so that its axis coincided with that of the latter. In observing the pressure on the gas in the thermometer, it was only necessary to read the difference of level between surfaces of the mercury in the dead-space and in the manometer tube which lay in the same vertical line. The top of the



manometer tube was 1500 millims. above the level of the dead-space, so that when the pressure on the gas in the thermometer was 1000 millims. there was still a considerable vacuous space above the mercury. The manometer tube was boiled out and the apparatus filled with mercury before the thermometer was fixed to its stand, or the bulb sealed to the capillary tube leading to the dead-space. For this purpose the apparatus was set up temporarily in clamps, and the top of the manometer tube, which was drawn out to a fine capillary (fig. 4, A), was sealed to a tube leading to the mercury pump. The capillary tube connected with the dead-space was also closed.

After thoroughly exhausting the apparatus, and heating it to remove trace of water condensed on the glass, mercury was admitted through the stop-cock *n*. As the mercury entered the manometer tube it was boiled by heating the tube with a Bunsen burner. By this method, which we have frequently employed, the rising surface of the mercury remains in contact with mercury vapour only, and as the exhaustion is continued throughout the operation a very perfect barometric vacuum is finally obtained. By admitting air to the tube *h* through the stop-cock *i*, and lifting the reservoir attached to the tube *l*, the mercury in the manometer tube was raised nearly to the top. By heating, mercury vapour was made to pass through the constriction, and condense in the descending tube. The constriction was then heated in the blow-pipe, and the manometer was sealed. The mercury was then allowed to fall in the manometer tube.

The bulb was not sealed to the rest of the apparatus till this operation had been completed, as it was found that it was impossible to prevent mercury vapour condensing in it. The connection was now made by sealing the stem with a mouth blow-pipe. It was unnecessary to make any correction for the distortion of the stem, as the volume of 1 millim. of its length amounted only to 0.000444 cub. centim.

The instrument was now fixed to its permanent support, as in fig. 4. This consisted of a stout wooden plank, 3 centims. thick and 15 centims. wide at the bottom, cut away for 6 centims. of its width from the level of the dead-space upwards to allow of the illumination of the scale from behind. The support was stayed rigidly at the top to the wall and to a beam running transversely across the room, so as to prevent all lateral movement.

We do not intend to give an account of the experiments which we carried out before we commenced the series of measurements on which we base our results. It will suffice to state that about four months were spent detecting and eliminating sources of error such as that due to lack of rigidity in the apparatus.

## 12. *Introduction of the Gas into the Apparatus.*

The gases employed in these experiments were hydrogen and helium, and it will be convenient to consider the method by which they were prepared and purified at a later stage. The gas was introduced into the thermometer through the stop-cock *i*,

which for this purpose was connected through a bulb  $x$  and a tube  $z$  to the apparatus containing the gas, and to a mercury pump. The tube  $x$  was intended to receive the mercury contained in the portion of the side tube above the stop-cock.

By lowering the reservoir connected by the rubber tube  $l$  with the stop-cock  $n$ , the level of the mercury in  $h$  could be made to fall below the point of entry of the side tube connected with  $i$ . Then by carefully opening the cocks  $i$  and  $n$  alternately and manipulating the mercury pump, the gas in the apparatus could be completely removed. When this was effected the mercury in the tubes  $h$ ,  $g$ , and  $k$  stood at the same level. Before introducing the gas the bulb was heated in an air-bath for about an hour to  $150^{\circ}$  C. to move all traces of moisture, and was washed out several times with the dry gas.

The operation of filling the apparatus was the reverse of that of emptying it. The gas was admitted slowly by opening the stop-cock  $i$ , and at the same time mercury was admitted through the stop-cock  $n$ . The quantity of gas required to fill the apparatus to the desired pressure was at first found by trial, but after the first experiment it was known that when the level of the mercury in the tube  $h$  lay just below the tube leading to  $i$ , the mercury rose to a certain height in the manometer tube  $g$ . When sufficient gas had been admitted the stop-cock  $i$  was closed and more mercury was allowed to enter the apparatus through  $h$ . The gas in the portion of the side tube above  $i$  was easily displaced by mercury. (See also Part III., p. 171, *et seq.*)

### 13. *The Scale.*

The measurement of the pressure in the thermometer bulb could have been easily and effectively made by employing a well constructed cathetometer with a standard scale attached to it. As, however, we had no means of obtaining such an instrument, we were obliged to employ the following method.

On the surface of a piece of plate-glass short scales ruled in millimetres by ZEISS of Jena, were cemented by means of Canada balsam. The scale so constructed was fixed in front of the mercury column and dead-space, so that when the lowest scale, which was 50 millims. in length, was in front of the dead-space, the four remaining scales were 100 millims. in length. With this arrangement it was possible to fill the thermometer at three initial pressures, viz., at 350, at 500, and at 700 millims. of mercury, and to determine the pressure coefficient of the gas at each pressure. The method of observation will be described later.

The distances between the points on the scale at which observations were made were first of all determined by us by means of a micrometer apparatus, designed by Mr. HILGER for measuring spectro-photographs, with a screw of 1-millimetre pitch and a drum divided into 100 parts. By means of this instrument it was possible to determine lengths of 150 millims. to 0.002 millim. At the end of our research the

scale was sent to the National Physical Laboratory, and was there compared with a standard brass metre scale (Société Genevoise, No. 59); the comparison was guaranteed to 0.01 millim. For this we wish to express our thanks to the Director, Mr. R. T. GLAZEBROOK.

The results of the two sets of comparison are very concordant, except so far as the distance between scale I. and scale III. is concerned. With regard to the discrepancy of 0.015 millim. which exists here, we wish to state that the values of the pressure-coefficients first obtained for hydrogen at initial pressures of 350 and 500 millims., indicated that there was probably a small error in the scale at this point. This has been corrected.

In the following table column A gives the distances between the line 9 on the lowest scale (I.) and the middle points on the four remaining scales, as determined by us; column C gives the value stated in the certificate furnished by the National Physical Laboratory, while the numbers in column B are calculated from those in column C by multiplying the latter by the factor  $962.395/962.28$ .

	A.	B.	C.
Line 9, scale I., to line 50, scale II. . . .	369.895	369.895	369.85
"      "      "      "      III. . . .	521.505	521.52	521.46
"      "      "      "      IV. . . .	684.644	684.64	684.56
"      "      "      "      V. . . .	962.395	962.395	962.28

It need not be pointed out here, that in the measurements of the pressure-coefficient it is only necessary to know the absolute length of the scale approximately. We have accordingly taken the figures in the second column (B) as representing the distances between the standard points on our scale.

#### 14. *The Temperature of the Mercury Column.*

Since in these experiments we were attempting to measure the pressure with a degree of accuracy approaching 0.01 millim., it was necessary to take special precaution with regard to the temperature of the mercury column. In our first experiments we attempted to measure the temperature of the column by means of four thermometers, the bulbs of which were enclosed in glass tubes, of the same diameter as the barometer column, filled with mercury. We found, however, that the temperature could not be read with certainty to 0.2 C., nor even with that degree of accuracy when the steam point was being determined. As an error of 0.01 in the temperature of the column involves a corresponding error of 0.016 millim. in  $P_{100}$  (950 millims.), we enclosed the dead-space and mercury columns in a water jacket.

The manner in which this was effected is shown in fig. 4. The dead-space and manometer column were enclosed between two pieces of plate-glass,  $p$  and  $o$ , the pieces of plate-glass  $p$  in front forming the scale; strips of wood,  $r$  and  $r'$ , formed the side and bottom of the water jacket, the whole being made water-tight by means of a mixture of red-lead and gold size. The arrangement was carried on brass brackets  $ss$  screwed to the face of the main support. The two plates of glass were clamped to the wooden strips  $rr'$  by brass bands  $tt'$  and wooden wedges  $uu'$ ; the brass bands were screwed at one end to the main support. Water entered the jacket at the bottom, and escaping at the top by a rubber tube, flowed over the tubes  $h$  and  $k$ , and the portion of  $g$  below the water jacket. This part of the apparatus was swathed in cotton cloth, and was maintained at a constant, though indefinite temperature, by means of the current of water. The temperature of the water in the jacket remained constant within  $0^{\circ}02$  for a sufficient time for the measurement of the pressure, and rarely varied by  $0^{\circ}1$  during the period of one hour, necessary for four consecutive observations. The error due to temperature on  $P_{100}$  (950 millims.) is thus reduced to 0.002 millim. which is considerably less than the error of observation. It may also be noted here that, as the temperature of the dead-space was made with the same degree of accuracy, and an error of 0.1 in determining it makes a difference of 0.002 millim. on  $P_{100}$ , this source of error also disappears.

The height of the column of which the temperature varied between  $8^{\circ}$  and  $17^{\circ}$  C. was reduced in every case to the height at  $10^{\circ}$  C.

It is obvious that as the manometer tube and the glass scale in front of it are not parallel, and the space between them is filled with water, a refraction error may be introduced which will have a constant influence on the value of  $P_0$  and  $P_{100}$ . If the deviation of the manometer tube amounts to 2 millims. in its total length, the error in reading the height of the column would be roughly 0.01 millim. By observing the height of the column when the jacket contained water, and then allowing the water to escape rapidly, we could, however, detect no change in the position of the meniscus. Further, since the manometer tube was sufficiently straight for the error to affect  $P_0$  and  $P_{100}$  equally, the error due to refraction can be neglected.

#### 15. *The Measurement of the Pressure on the Gas in the Thermometer.*

The observations were made by means of a telescope placed at a distance of one metre from the scale. The telescope was fitted with a Hilger ocular micrometer, with a screw, divided into 100 parts, each corresponding to a movement of the cross-wire of 0.005 millim., or to 0.007 millim. on the scale. Each meniscus was illuminated from behind by means of an electric glow-lamp covered with white tissue paper; cards placed behind the glass plate  $O$ , cut off the light at a height of 1 or 2 millims. above the level of the mercury (*cf.* p. 109).

When the temperature of the bulb and column were steady, the mercury in the dead-space was adjusted first of all by means of the mercury reservoir and stop-cock *n*, and finally by means of the pinch-cock *m*. The mercury was always brought to within about 0.1 millim. of the point. After tapping the support with the hand, and waiting a short time for the mercury to settle down, the observations were made.

The spider-line of the micrometer was first brought into coincidence with the line on the scales next above the meniscus, and then with the top of the meniscus itself, readings being taken in both positions. A light was then held in front of the instrument, and the height of the meniscus was determined by bringing the spider line into coincidence with the point at which the vertical bright line, caused by the reflection of the light from the curved surface of the mercury column, came to an end. The height of the mercury meniscus was applied to the calculation of the correction to be applied for capillarity (KOHLRAUSCH). The determination of the position of the point *e* with regard to the scale was also necessary for the calculation of the distance of the mercury from it, and from this the volume of the dead-space. Its value, and the value of one division of the micrometer screw in terms of a division of the scale, were measured separately.

Observations of the pressure were invariably made by each one of us alternately, the other reading the thermometer enclosed in the water jacket, and the thermometer placed close to the horizontal portion of the stem. The position of the lower meniscus was observed, then that of the upper meniscus, and finally the lower meniscus again. The level of the mercury in the apparatus was usually readjusted between each pair of measurements.

#### 16. *The Ice-Point.*

The bulb was immersed to within 40 millims. of the horizontal portion of the stem in an inverted glass bell-jar, and surrounded with broken ice packed tightly round it. The bell-jar was filled nearly to the top of the vessel with distilled water. Samples of the ice were on two occasions melted and the liquid evaporated; in neither case was it found to contain more than a minute trace of solid matter. A piece of wood, with a slit cut in it for the stem of the thermometer, was placed on top of the bell-jar containing the ice.

#### 17. *The Boiling-Point.*

The bulb of the thermometer was surrounded with dry steam by means of a large double-walled copper hypsometer of the usual form. The stem of the thermometer passed through a hole in the cover of the hypsometer, and the aperture was made fairly steam-tight by means of a small strip of wet rag wound round the stem. No correction of the difference of pressure inside and outside the hypsometer was necessary.

To shield the apparatus against radiation from the heated vessel a piece of wood, kept wet by a stream of water, was used as a screen. A similar piece of wood, with a slit cut in it for the stem, was held in a clamp horizontally about 1 centim. above the top of the hypsometer to screen the horizontal portion of the stem. The temperature of the short length of stem between the hypsometer and the screen was usually about  $96^{\circ}$ , a difference from  $100^{\circ}$  too small to be considered. During each experiment the barometer was always read three times; at the beginning, at the end, and between the two pairs of observations.

### 18. *Calculation of the Results.*

In calculating the value of the pressure coefficient from the results of our experiments, we employed the usual methods. The pressure  $P_0$  and  $P_{100}$  which the gas would exert at the temperature of melting ice, and at that of saturated water vapour at the normal pressure, if confined in a space corresponding to the volume of the thermometer at  $0^{\circ}$  C., were first calculated. The pressure coefficient was then obtained from the equation

$$\alpha = (P_{100} - P_0)/100 P_{100}.$$

In calculating  $P_0$  and  $P_{100}$  it is of course necessary to assume some value for the pressure coefficient in order to apply the necessary correction for the gas contained in the stem and dead-space; and in reducing the temperature of the bulb to  $100^{\circ}$  C. in calculating  $P_{100}$ . These corrections are, however, small; and no appreciable error is introduced by taking the coefficient as  $1/273$ .

The following equations were employed in calculating  $P_0$  and  $P_{100}$  :—

$$P_0 = P \left\{ V_b + \frac{V_s \times 273}{273 + T_s} + \frac{V_{ds} \times 273}{273 + T_{ds}} \right\} \frac{1}{V}$$

$$P_{100} = P' \left\{ \frac{V_b' \times 373}{273 + T} + \frac{V_s \times 373}{273 + T_s'} + \frac{V_{ds} \times 373}{273 + T_{ds}'} \right\} \frac{1}{V}.$$

Where  $P$  is the observed pressure at the ice-point.

$P'$  is the observed pressure at the steam-point.

$T$  is the temperature of steam corresponding to the barometric pressure.

$T_s$  and  $T_s'$  are the temperatures of the stem.

$T_{ds}$  and  $T_{ds}'$  are the temperatures of the dead-space.

$V_b$  is the volume of the bulb at the ice-point.

$V_b'$  is the volume of the bulb at the steam-point.

$V_s$  is the volume of the stem.

$V_{ds}$  is the volume of the dead-space.

$V = (V_b + V_s + V_{ds})$ , is the total volume of the thermometer at  $0^{\circ}$  C.

The method by which the temperature, pressure, and volume were calculated and corrected has already been dealt with.

19. *Details of the Results of One Experiment.*

As we have already stated, each determination of the ice-point or boiling-point consisted of four separate observations of the height and temperature of the barometer column, of the temperature of the stem, &c. The readings were taken by each of us alternately. In determining the boiling-point the barometer was also read three times, at the beginning, at the end, and in the middle of each set of experiments, and the temperature of the bulb was calculated from the mean corrected pressure. It would be useless to set down the whole of the measurements involved in every experiment, but in order to give an idea of the accuracy of the observations, we give the full details of one complete set of measurements.

## Ice-Point, February 24th, 1902.

	I.		II.		III.		IV.	
	Micrometer readings.	Mean in millims.	Micrometer readings.	Mean in millims.	Micrometer readings.	Mean in millims.	Micrometer readings.	Mean in millims.
Lower meniscus { Line 9 to point Line 9 to meniscus Height of meniscus	67, 67, 68	0.469	73, 73, 70	0.504	77, 78, 77	—	69	0.483
	80, 80, 80	0.560	80, 80, 78	0.563	181, 181, 184	0.539	74, 75, 78, 79	0.539
	177, 178	1.25	180, 180	1.26	100, 100	1.27	185, 180	1.27
Upper " { Line 60 to meniscus Height of meniscus	102, 102	0.714	98, 99	0.689	144, 146	0.700	99, 99	0.693
	129, 132	0.98	140, 139	0.98	—	1.01	146, 144	1.01
Temperature of dead-space . . . . .	8.78° C.		8.76° C.		8.64° C.		8.60° C.	
" " stem . . . . .	19.1° C.		19.6° C.		19.6° C.		18.6° C.	

	I.		II.		III.		IV.	
Line 9 (lower scale) to line 60 (upper scale) . . . . .	694.644		694.644		694.644		694.644	
Δ bottom. . . . .	+0.560		+0.553		+0.539		+0.539	
Δ top . . . . .	-0.714		-0.689		-0.700		-0.693	
Temperature correction to 10° C. . . . .	+0.141		+0.143		+0.158		+0.162	
Correction for capillarity . . . . .	-0.081		-0.084		-0.078		-0.078	
Pressure in millims. of mercury at 10° C. . . . .	694.550		694.567		694.563		694.574	
Volume of dead-space. . . . .	0.3958		0.3959		0.3945		0.3945	

Mean pressure . . . . . 694.564 millims.  
 Mean volume of dead-space . . . . . 0.3950 cub. centim.  
 Mean temperature of dead-space . . . . . 8.70° C.  
 " " stem . . . . . 19.3° C.  
 P<sub>0</sub> . . . . . 694.458.



Boiling-Point, February 25th, 1902.

	I.		II.		III.		IV.	
	Micrometer readings.	Mean in millims.	Micrometer readings.	Mean in millims.	Micrometer readings.	Mean in millims.	Micrometer readings.	Mean in millims.
Lower meniscus { Line 9 to meniscus . { Height of meniscus .	78, 79, 79 185, 182, 177	0.553 1.27	78, 79, 79 185, 186	0.553 1.29	80, 78, 79 175, 178, 180	0.553 1.25	78, 79, 77 180, 180, 186	0.546 1.27
Upper " { Line 31 to meniscus . { Height of meniscus .	38, 39 158, 155	0.269 1.10	36, 39 157, 154	0.262 1.08	39, 39 150, 152	0.273 1.06	35, 35, 35 157, 159	0.247 1.11
Temperature of dead-space . . . . .	8.38° C. 27.0° C.		8.31° C. 27.1° C.		8.31° C. 27.1° C.		8.30° C. 27.0° C.	
" " stem (a) . . . . .	92.5° C.		92.0° C.		92.0° C.		92.0° C.	
" " " (b) . . . . .								

	I.		II.		III.		IV.	
	I.		II.		III.		IV.	
Line 9 (lower scale) to line 31 (upper scale) . . . . .	943.394		943.394		943.394		943.394	
Δ bottom . . . . .	+0.553		+0.553		+0.553		+0.546	
Δ top . . . . .	-0.269		-0.262		-0.273		-0.246	
Temperature correction to 10° C. . . . .	+0.253		+0.265		+0.265		+0.266	
Correction for capillarity. . . . .	-0.051		-0.063		-0.057		-0.051	
Pressure corrected to 10° C. . . . .	943.880		943.887		943.882		943.910	
Volume of dead-space . . . . .	0.3944		0.3944		0.3944		0.3940	
Observed height of barometer . . . . .	I. 754.11 millims.		II. 754.06 millims.		III. 754.06 millims.		17.8° C.	
Temperature of barometer . . . . .	16.8° C.		17.1° C.		17.1° C.			

Mean pressure . . . . .	943.889 millims.	Mean volume of dead-space . . . . .	0.3943
Volume of bulb . . . . .	94.4776 cub. centims.	Mean temperature of dead-space . . . . .	8.33° C.
Mean barometric pressure . . . . .	752.11	" " stem . . . . .	(a) 27.0°, (b) 92° C.
Temperature of steam . . . . .	99.709	P <sub>100</sub> . . . . .	948.824

## 20. The Pressure Coefficient of Hydrogen.

Series I. and II. at initial pressures of about 700 millims.

Series III.

Series IV.

Series V.

"	"	500	"
"	"	350	"
"	"	700	"

## I.) Hydrogen.

## Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
Feb. 24th	694·550, ·567, ·563, ·574	694·564	0·3949	° C. 8·70	° C. 19·3	694·458
Feb. 25th	694·524, ·542, ·563, ·581	694·552	0·3950	7·74	20·0	694·452

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem (a).	Mean temperature of stem (b).	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
Feb. 24th	943·755, ·731, ·765, ·773	943·756	0·3949	° C. 8·17	° C. 26·3	° C. 94	751·18	° C. 99·675	948·789
Feb. 25th	943·880, ·887, ·882, ·910	943·889	0·3944	8·33	27·0	92	752·11	99·709	948·824
Feb. 26th	943·640, ·674, ·662, ·671	943·665	0·3948	8·54	26·3	94	749·96	99·630	948·809

Mean P<sub>0</sub> 694·455. Mean P<sub>100</sub> 948·807.  $z = 0·00366261$ .

## (II.) Hydrogen.

## Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
Feb. 26th	696·178, ·186, ·200, ·225	696·198	0·3956	° C. 8·14	° C. 19·2	696·103
Feb. 27th	696·176, ·216, ·207, ·183	696·196	0·3958	8·37	17·7	696·102

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem (a).	Mean temperature of stem (b).	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
Feb. 27th	945·157, ·193, ·151, ·156	945·160	0·3975	° C. 8·15	° C. 26·1	° C. 87	742·37	° C. 99·346	951·059
Feb. 28th	945·687, ·716, ·713, ·736	945·713	0·3959	9·03	21·5	93	748·24	99·565	951·044

Mean P<sub>0</sub> 696·103. Mean P<sub>100</sub> 951·052.  $z = 0·00366252$ .

In these experiments the short length of the stem (*b*) outside the hypsometer was considered separately. No error is however, introduced by considering it to be heated to 100° C. The thermometer was completely exhausted and was refilled with hydrogen between the first and second series of experiments.

## (III.) Hydrogen.

## Ice-Point

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
March 4th	520·384, ·411, ·406, ·430	520·408	0·3950	° C. 9·94	° C. 16·4	520·326
March 5th	520·388, ·403, ·381, ·380	520·388	0·3952	9·53	15·3	520·311

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem (a).	Mean temperature of stem (b).	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
March 3rd	707·808, ·794, ·783, ·794	707·795	0·3965	° C. 9·06	° C. 25·0	° C. 92	761·27	° C. 100·046	710·897
March 4th	707·831, ·832, ·837, ·839	707·835	0·3966	9·46	25·2	68	761·71	100·062	710·882
March 5th	707·914, ·915, ·907, ·896	707·908	0·3954	9·42	24·7	85	762·41	100·087	710·907

Mean P<sub>0</sub> = 520·319.      Mean P<sub>100</sub> = 710·895.       $\alpha = 0·00366268$ .

## (IV.) Hydrogen.

## Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
March 6th	348·036, ·041, ·006, ·010	348·023	0·3952	° C. 9·55	° C. 18·7	347·968
March 11th	348·056, ·054, ·060, ·070	348·060	0·3947	9·74	17·6	348·002
March 11th	348·086, ·049, ·072	348·069	0·3949	9·17	19·0	348·009

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem (a).	Mean temperature of stem (b).	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
March 6th	473·403, ·417, ·404, ·397	473·405	0·3950	° C. 9·65	° C. 27·0	° C. 86	761·59	° C. 100·057	475·428
March 7th	473·294, ·295, ·286, ·288	473·291	0·3946	9·59	29·0	68	759·05	99·964	475·439
March 10th	473·342, ·333, ·334, ·331	473·335	0·3944	9·49	23·2	91	760·14	100·004	475·436

Mean P<sub>0</sub> = 347·993.      Mean P<sub>100</sub> = 475·434.       $\alpha = 0·00366133$ .

(V.) Before determining the pressure coefficient for helium, as a considerable time had elapsed since the measurements of the coefficients for hydrogen had been made, the thermometer was refilled with hydrogen, and an ice-point and a boiling-point were determined.

#### Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space. °C.	Mean temperature of stem. °C.	P <sub>0</sub> .
May 8th	706·604, ·622, ·649, ·623	706·663	0·3970	11·14	14·4	706·528

#### Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space. °C.	Mean temperature of stem. °C.	Barometric pressure.	Temperature of steam. °C.	P <sub>100</sub> .
May 7th	961·504, ·516, ·435, ·427	961·431	0·3986	11·26	21·3	765·18	100·189	965·291

$$P_0 = 706·528, \quad P_{100} = 965·291, \quad \alpha = ·00366246.$$

Since this value for the coefficient is the result of one observation of the ice-point and one of the boiling-point, it can only be taken as confirming our previous determination, and as indicating that our apparatus was still in thorough working order.

#### 21. *The Pressure Coefficient of Helium.*

Series I. and II. at initial pressures of about 700 millims.

Series III. and IV.       "       "       500       "

(I.) Helium. (For preparation of the gas see Part III., p. 171.)  
Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
May 29th May 30th	690·385, ·346, ·398, ·376 690·391, ·385, ·377, ·391	690·376 690·386	0·3976 0·3950	°C. 15·11 15·48	°C. 17·6 18·7	690·232 690·238

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
May 29th May 30th May 31st	938·548, ·507, ·524, ·509 938·174, ·154, ·164, ·133 938·208, ·200, ·220, ·196	938·522 938·154 938·206	0·3996 0·3964 0·3987	°C. 15·13 15·40 15·33	°C. 22·8 22·0 24·1	755·54 751·86 753·21	°C. 99·863 99·700 99·750	943·044 943·044 942·992

Mean P<sub>0</sub> = 690·235. Mean P = 943·027.  $\alpha = 0·00366241$ .(II.) Helium. (A small quantity of gas was removed from the bulb between Experiment I. and II.)  
Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
June 2nd June 3rd	671·582, ·559, ·589, ·565 671·580, ·563, ·587, ·566	671·574 671·574	0·3977 0·3957	°C. 15·98 16·10	°C. 19·1 19·2	671·422 671·408

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
June 2nd June 3rd June 4th	913·602, ·588, ·573, ·601 913·511, ·510, ·511, ·503 913·428, ·476, ·485, ·515	913·591 913·509 913·476	0·3974 0·3953 0·3977	°C. 15·94 16·10 16·49	°C. 20·8 22·2 22·5	763·22 762·41 761·96	°C. 100·118 100·089 100·072	917·352 917·322 917·328

Mean P<sub>0</sub> = 671·415. Mean P<sub>100</sub> = 917·334.  $\alpha = 0·00366270$ .

## (III.) Helium at lower pressure.

## Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
June 5th	523·108, ·098, ·117, ·118	523·108	0·3964	° C. 16·15	° C. 17·85	522·984
June 6th	523·081, ·098, ·111, ·119	523·108	0·3962	16·02	18·6	522·984

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
June 5th	711·598, ·581, ·595, ·611	711·599	0·3967	° C. 17·43	° C. 24·1	761·96	100·072	714·576
June 6th	711·244, ·242, ·234, ·231	711·238	0·3969	16·09	23·5	757·73	99·917	714·529
June 7th	710·632, ·602, ·620, ·581	710·594	0·3947	15·62	22·8	747·76	99·548	714·577

Mean P<sub>0</sub> = 522·984.      Mean P<sub>100</sub> = 714·560.       $\alpha = 0·00366313$ .

## (IV.)

## Ice-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	P <sub>0</sub> .
June 16th	523·120, ·122, ·116	523·119	0·3957	° C. 13·40	° C. 15·1	523·016
June 17th	523·147, ·130, ·129, ·121	523·132	0·3939	13·40	15·2	523·020

## Boiling-Point.

Date.	Observed pressure, corrected.	Mean pressure.	Mean volume of dead-space.	Mean temperature of dead-space.	Mean temperature of stem.	Barometric pressure.	Temperature of steam.	P <sub>100</sub> .
June 16th	710·987, ·967, ·973, ·985	710·978	0·3929	° C. 13·48	° C. 20·5	753·46	99·759	714·568
June 17th	711·436, ·423, ·453, ·438	711·438	0·3940	13·38	19·7	760·12	100·005	714·583

Mean P<sub>0</sub> = 523·018.      Mean P<sub>100</sub> = 714·576.       $\alpha = 0·00366255$ .

22. *Accuracy of the Results.*

In describing the construction of the apparatus and the manner in which the experiments were carried out, we have already pointed to the errors which may occur and their effect on the accuracy of the final result. It will have been noticed that with the exception of the errors in the barometer reading, and in the temperature of the steam in the hypsometer, the errors of observation affect  $P_0$  and  $P_{100}$  almost equally, and hence have little effect on the value of the coefficient. Further, since an error of 0.1 millim. in the barometer reading only changes the value of  $P_{100}$  (950 millims.) by 0.003 millim., the effect of such an error on the value of the coefficient is less than five units in the sixth significant figure.

With regard to the measurement of the pressure, as we have already stated, the errors in the scale were certainly less than 0.01 millim. An error in the difference  $P_{100}-P_0$  of this magnitude would involve an error of one unit in the fifth significant figure. The actual extreme difference between the value of  $P_{100}$  in the set of three observations which constitute each series usually amounts to 0.02 to 0.03 millim., but these differences appear to be unbiassed and do not influence the final result in one direction or in the other. The value of the temperature correction practically disappears, for, as we have pointed out, the temperature of the column could be determined to 0.02° C., and in successive determinations of  $P_0$  and  $P_{100}$  the temperatures were practically identical. The capillarity correction involving the height of the meniscus we considered at first to have a doubtful character, but as the height of the meniscus varied by 0.04 millim. in different observations, and the application of the correction brought the observed pressures to the same value, we have come to the conclusion that it is sound.

The errors in the measurement of the volume and temperature of the dead-space are small. Their effect on the value of the coefficient has already been sufficiently discussed.

23. *The Final Values for the Pressure Coefficients of Hydrogen and Helium.*

As the tables in Sections 20 and 21 show, we have two series of determinations of the pressure coefficient both in the case of hydrogen and of helium at initial pressure of about 700 millims. of mercury. The results are as follows:—

Gas.	Observed values of the coefficient, $\alpha$ .		Mean value.
Hydrogen . . . . .	0.00366261,	0.00366252	0.00366255
Helium. . . . .	0.00366241,	0.00366270	0.00366255

Each of the observed values is based, as the tables show, on eight measurements of the pressure on the gas, the temperature of the dead-space, &c., when the bulb of the thermometer was immersed in ice, and twelve similar measurements where the bulb was surrounded with steam. The agreement between the observations is satisfactory.

As has already been pointed out at the commencement of this paper, the best determinations of the pressure coefficient for hydrogen are those of CHAPPUIS and ONNES. CHAPPUIS' work is to be found in the 'Travaux et Mémoires du Bureau International des Poids et Mesures,' vol. 6 (1888), and in the subsequent volumes; an account of his work is also to be found in the 'Rapports du Congrès International de Physique' (Paris, 1901). The results obtained in 1887 with his large thermometer, which has a platinum-iridium bulb of nearly 1 litre capacity filled at an initial pressure of 1000 millims. of mercury, are as follows :—

Value of the coefficient.	Mean values.
0·00366271	} 0·00366254
0·00366248	
0·00366225	
0·00366231	
0·00366256	
0·00366270	
0·00366269	

The mean value of four determinations carried out in 1899 with the same thermometer was 0·00366296, and of five determinations made in 1895 with a bulb of "verre dur" was 0·00366217. The mean value of the seven determinations made in 1887 is, however, retained as the probable value of the coefficient, which forms the basis for the definition of the so-called normal scale of temperature.

The three determinations of the coefficient by ONNES ('Communications from the Physical Laboratory of the University of Leiden,' No. 60) are as follows :—

$$0\cdot0036628, \quad 0\cdot0036624, \quad 0\cdot0036628.$$

As in the case of CHAPPUIS' experiments, the initial pressure in the thermometer was about 1000 millims. of mercury.

Though the highest initial pressure at which our measurements were made was 700 millims. of mercury, there is, as we shall presently show, no reason for assuming that the coefficient varies with the pressure, and the agreement between CHAPPUIS' results and our own may be considered as confirmatory of the latter. The combined results may probably be considered correct to the fifth significant figure.



*24. The Pressure Coefficients of Hydrogen and Helium at Lower Initial Pressures.*

Though the accuracy of the determinations of the pressure coefficients at lower pressures is reduced in proportion to the initial pressure, the results we have obtained indicate that the pressure coefficient for the two gases is practically independent of the pressure. The value of the coefficient found for hydrogen at an initial pressure of 500 millims. is 0·0036627, and for helium 0·0036625 and 0·0036631; if the coefficient attained a limiting value corresponding to 0·003660 at zero pressure, the value at 500 millims. should be 0·0036612.

The determination of the pressure coefficient for hydrogen at an initial pressure of 350 millims. is practically valueless; only one set of measurements was made, and we found that our method was not sufficiently accurate to investigate the coefficient at such a low pressure.

*25. General Conclusions.*

CHAPPUIS has determined the pressure coefficients of nitrogen at different pressures with the following results:—

Initial pressure.	Coefficient.
millims.	
1000	0·00367445
793·5	0·0036718
530·8	0·0036683

On plotting the values of the coefficient against the initial pressure, the value of the coefficient at zero initial pressure is found on linear extrapolation to lie between 0·003662 and 0·003663.

As DANIEL BERTHELOT ('Comptes Rendus,' 1898) has pointed out, the specific volumes of the common gases at zero pressure, calculated from their densities under normal conditions, and the variation of "p.v." with pressure, are the same. Their densities under the same conditions are proportional to their chemical atomic weights. If this is the case, they should, at zero pressure, behave as perfect gases, and the temperature scale on a thermometer filled with any gas at very low pressure should be coincident with the absolute scale of temperature.

If our conclusion is correct, that the pressure-coefficient for hydrogen and for helium has the value 0.00366255, and is independent of the pressure below 1000 millims. of mercury, it is probable that the melting-point of ice on the absolute scale does not lie very far from  $273^{\circ}03$ . Before we can apply ROSE-INNES' equations (*loc. cit.*, p. 106) to the investigation of the problem, it will be necessary, however, to obtain a more complete knowledge of the thermo-dynamic properties of these gases.

## PART II.

*On the Vapour Pressures of Liquid Oxygen at Temperatures below its Boiling-Point  
on the Constant-Volume Hydrogen and Helium Scales.*

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1. *Introduction.*

AFTER determining the pressure coefficients of hydrogen and helium between the melting-point of ice and the boiling-point of water, and so obtaining the fundamental intervals of our thermometer scales, we proceeded to apply our results to the determination of the boiling-point and vapour pressures of liquid oxygen. In these experiments we have employed three different thermometers; the coefficient of expansion of the glass at low temperatures has been specially determined; every precaution has been taken in preparing the different samples of hydrogen and helium employed; and the errors due to impurity in the oxygen and to the superheating of the liquid have, we believe, been eliminated. The following account contains full details of our experimental method and results.

## 2. *Previous Measurements of the Vapour Pressures of Liquid Oxygen.*

The earliest measurement to which any importance can be attached is that of WROBLEWSKI in 1888 ('Wiener Berichte,' 97, Abth. 2A, p. 1321). The temperature of the boiling-point of oxygen was measured on the constant-volume hydrogen scale, but no details are given in the paper, which is entitled "Die Zusammendrückbarkeit des Wasserstoffs," and was published after his death. The number given by him is  $182.4^{\circ}\text{C}$ .

OLSZEWSKI appears to have measured the boiling-point of oxygen on several occasions. In 1896 he published in 'Nature' (vol. 54, p. 377) an account of his comparison of the hydrogen and helium thermometers at temperatures corresponding to vapour pressures below 741 millims. mercury. By extrapolation the temperature of the boiling-point on either thermometer appears to be  $-182.36^{\circ}\text{C}$ . In his paper on the liquefaction of gases ('Phil. Mag.,' 1895, vol. 39, p. 188) he gives  $-181.4^{\circ}$  as the boiling-point. The capacity of the bulb of his thermometer was only 2 cub. centims.

ESTREICHER ('Phil. Mag.,' (5), vol. 40, p. 454) also made a large number of measurements. He made twenty-five measurements of the temperature corresponding to 744.8 millims., and gives  $-182.56^{\circ}\text{C}$ . as the mean of the results. The boiling-point calculated by extrapolation is  $-182.4^{\circ}\text{C}$ . ( $\Delta T$  being  $0.0122^{\circ}$  per millimetre). ESTREICHER worked in OLSZEWSKI's laboratory, and employed the same instrument as the latter.

WITKOWSKI ('Phil. Mag.,' 1896, vol. 42) gives the boiling-point of oxygen as  $-182.446^{\circ}\text{C}$ ., employing the value 0.00366 for the coefficient of expansion of hydrogen.

HOLBORN and WIEN ('Wied. Ann.,' 1896, vol. 59, p. 213) compared the hydrogen and air thermometers at the temperature of liquid air, and found that the readings of the air thermometer were  $0.65^{\circ}$  lower than those of the hydrogen thermometer. Later, HOLBORN ('Ann. der Physik,' (4), 1901, vol. 6, p. 242) standardised a platinum resistance thermometer by means of an air thermometer, and by means of it measured the boiling-point of pure oxygen. The temperature referred to the constant-volume hydrogen scale is  $-182.7^{\circ}\text{C}$ . Full details of the work, which was carried out in the Physikalische Reichsanstalt at Charlottenburg, are given in the paper.

LADENBURG and KRUGEL ('Ber.,' 1900, vol. 32, p. 1818, vol. 33, p. 637) found  $-182.2^{\circ}$  for the temperature corresponding to a pressure of 745 millims. (boiling-point  $-182.05^{\circ}\text{C}$ .). The measurement was made by means of a thermo-electric junction, standardised at the temperature of liquid air, which was supposed to be  $-191.25^{\circ}$ .

DEWAR ('Proc. Roy. Soc.,' 1901, vol. 68, p. 44), employing constant volume thermometers filled with hydrogen and oxygen, obtained the following values. The numbers in third value of the following table are calculated from the mean value of  $dp/dt$ .

## Hydrogen Thermometer.

Pressure.	Temperature.	Boiling-point; calculated.
	° C.	° C.
760·6	-182·20	-182·21
764·4	-182·67	-182·72
759·5	-181·62	-181·52

The coefficient of expansion for hydrogen is taken as 0·0036625. Taking the same coefficient for oxygen, a proceeding which does not appear to be justified, he obtained the following results :—

## Oxygen Thermometer.

Pressure.	Temperature.	Boiling-point; calculated.
	° C.	° C.
772·5	-182·29	-182·43
756·0	-183·46	-183·42
753·5	-182·95	-182·90

BALY ('Phil. Mag.,' 1900, vol. 49, p. 517) measured the vapour pressures of oxygen on the constant-pressure hydrogen scale, employing a Callendar thermometer. The results appear to be affected by a constant error; they will be discussed elsewhere.

So far as the evidence contained in the original papers is concerned, it appears to us that greatest weight is to be attached to the work of HOLBORN and WIEN. It is true that the results of WROBLEWSKI, OLSZEWSKI, and ESTREICHER show a close agreement, but none of these experimentalists furnish sufficient data to make criticism possible.

In all the experiments we have referred to, the boiling-point or vapour pressure of oxygen has been measured by immersing the thermometer in the liquid and measuring the pressure at which it was boiling. ESTREICHER and OLSZEWSKI measured the vapour pressures at lower temperatures by connecting the vacuum vessel containing the liquid with an exhaust pump, and making the liquid boil under reduced pressure.

The difficulty of making accurate measurements by this method is twofold. In the first place, it is not easy to liquify a sufficient quantity of pure oxygen; and in the second place, the liquid oxygen tends to become superheated, and does not boil steadily. The impurity in the oxygen would most probably be air, which would lower the boiling-point; other impurities would, however, have the opposite effect.

In every case it appears to have been assumed that the coefficient of expansion for glass remains constant over the whole range of temperature.

### 3. *The Pressure Coefficients of Hydrogen and Helium between 0° and 100° C.*

As has already been pointed out, there is no appreciable difference between the pressure coefficient of the two gases, which may be considered as approximating very closely to 0.00366255. The reciprocal of this number is 273.03, and though an error of 0.01° only is incurred by taking 273 as the temperature of melting ice on the scale of either thermometer, we have in calculating our results employed the true coefficient.

### 4. *The Coefficient of Expansion of Glass between 16° and — 190° C.*

The coefficient of expansion of the glass was determined in the following manner. The inner tube of a cylindrical vacuum vessel, which was 30 millims. wide and 1000 millims. long, was graduated for short distances close to its two ends. The vacuum vessel was enclosed in a water-jacket, and was set up vertically in front of two telescopes, of short focus, fitted with micrometer eye-pieces. The cross wires of the micrometer eye-pieces were first brought into coincidence with marks at the two ends of the vacuum vessel. The vessel was then filled with liquid air and the distances through which the marks on the vacuum vessel moved were observed. The following result for the volume coefficient is calculated from the linear contraction of the glass :—

Coefficient of expansion 0° to 100° C. (by weight thermometer)	. 0.0000285.
„ „ 0° to — 190° C. (from linear contraction)	. 0.0000218.

### 5. *Method of Experiment.*

In our experiments we have overcome the difficulty last referred to by immersing our thermometer, together with a bulb in which pure oxygen could be liquefied, and which was connected with a manometer, in liquid air or oxygen contained in a vacuum vessel. The liquid in the vacuum vessel could, if necessary, be made to boil steadily, by passing through it a current of air or hydrogen, and could be maintained at a constant temperature by enclosing the vacuum vessel in another vacuum vessel of larger dimensions also containing liquid air. Readings of the thermometer and of the manometer connected with the bulb containing the pure liquid oxygen were taken simultaneously by two observers.

### 6. *The Large Constant-Volume Thermometer.*

The thermometer employed in determining the pressure coefficients of hydrogen and helium between 0° and 100° C. has been fully described in the previous memoir (Part I.). The same instrument, and three others of smaller dimensions, were

employed in these researches, the larger thermometer being only used to determine four points on the vapour-pressure curve for liquid oxygen on the hydrogen scale as a check on the measurements made by means of the smaller instruments. It will be remembered that in the large instrument the mercury column and dead-space were enclosed in a water-jacket, and the pressure was measured by means of a scale of special construction, which formed the first surface of the water-jacket.

In these measurements the bulb of the thermometer and about 20 millims. of the stem were immersed in a liquid, consisting mainly of oxygen, contained in a vacuum vessel holding about 450 cub. centims., which was enclosed in a larger vacuum vessel containing a little liquid air. Beside the thermometer was placed, as in fig. 1, a glass tube *m*, in which pure oxygen, obtained by heating potassium permanganate, could be liquefied. This tube communicated with the pump, with the apparatus for generating the oxygen, and with a manometer of the type shown in fig. 2. During an experiment a stream of hydrogen was passed through the liquid in the inner vacuum vessel, to prevent superheating, and to stir it thoroughly.

In calculating the results it was possible to consider the whole of the stem from the top of the bulb to the level of the top of the vacuum vessel as at the temperature of liquid air. The portion not immersed in the liquid was only about 30 millims. long, and the error so introduced would be considerably less than  $0.01^{\circ}$  C. The coefficient of expansion of the glass between the freezing-point of water and the temperature of liquid air was taken as 0.0000218, a number which we obtained by actual experiment (p. 138). The thermometer was filled with pure dry hydrogen by the method described in the second appendix to Part III. of this paper.

The freezing-point of water on the constant-volume hydrogen scale is taken as 273.03, the reciprocal of the pressure coefficient 0.00366255.

The formula employed in calculating the results is as follows :—

$$P_0 \left\{ \frac{V}{273.03} + \frac{V_s}{273 + T_s} + \frac{V_{ds}}{273 + T_{ds}} \right\} = P \left\{ \frac{V(1 - \alpha(273 - T))}{T} + \frac{V_s}{273 + T'_s} + \frac{V_{ds}}{273 + T'_{ds}} \right\}$$

where  $P_0$  is the pressure on the gas when the bulb is surrounded with melting ice;  $P$  is the pressure on the gas when the bulb is at the temperature to be measured;

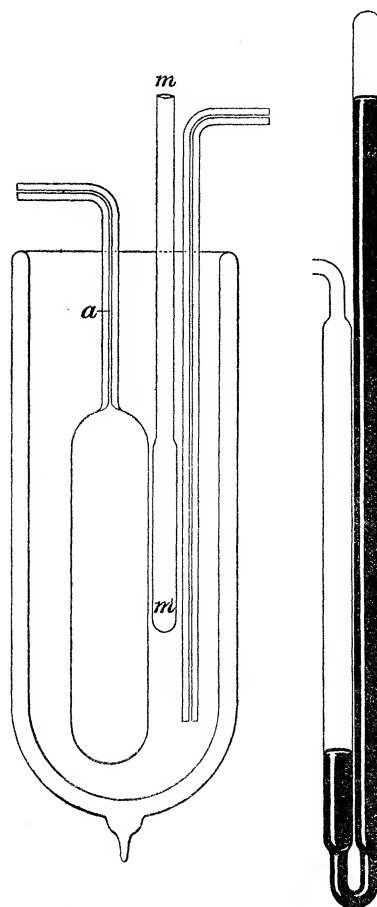


Fig. 1.

Fig. 2.

$V$  is the volume of the bulb to  $a$  (fig. 1), at  $0^\circ \text{C.}$ ;  $V_{ds}$  is the volume of the dead-space and the portion of the stem within the water-jacket;  $V_s$  is the volume of the remaining portion of the stem;  $\alpha$  is the coefficient of expansion of glass;  $T$  is the temperature to be measured;  $T_s T'_s$  and  $T_{ds} T'_{ds}$  are the temperatures of the stem and dead-space respectively in degrees Centigrade. The left-hand side of the equation gives the value of the constant for the thermometer.

#### The Ice-Point.

Volume of bulb at $0^\circ \text{C.}$ . . . . .	94.2096 cub. centims.
„ „ dead-space . . . . .	0.3904 „ „
„ „ stem . . . . .	0.1031 „ „
Pressure on gas corrected to $0^\circ \text{C.}$ . . . . .	987.00 millims.
Temperature of dead-space . . . . .	$11.29^\circ \text{C.}$
„ „ stem . . . . .	$17.4^\circ \text{C.}$
Constant . . . . .	342.235.

#### The Vapour Pressures of Liquid Oxygen.

Volume of bulb at $86.5 \text{ abs.}$ . . . . .	93.8336.
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Pressure on gas in thermometer, corrected to $0^\circ \text{C.}$	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid oxygen.	Temperature	
				Found.	From curve (p. 151).
	$^\circ \text{C.}$	$^\circ \text{C.}$	millims.	abs.	abs.
315.17	11.1	17.1	514.5	85.63	86.54
315.26	11.1	17.1	516	86.66	86.56
315.40	11.1	17.1	518.5	86.70	86.61
315.59	11.1	17.1	519.5	86.75	86.64

The figures in the last columns are obtained from the smoothed results of the measurements of the vapour pressure of oxygen obtained by means of the small thermometer. There appears to be a constant difference of  $0.1^\circ \text{C.}$

In discussing the accuracy of the result it is necessary to point out first of all that it is extremely difficult to maintain a large mass of liquid air or oxygen in a steady state of ebullition; and for this reason it is probable that the results obtained by means of the smaller thermometers are the more accurate. In the case of liquid air we have to deal not only with the difficulty which arises from the superheating of the liquid, but, as the liquid evaporates, its temperature rises rapidly. Liquid oxygen is not easy to obtain in large quantities, and it is extremely difficult to make it boil steadily; it may, in fact, become superheated to the extent of a whole degree Centigrade.



In the determination of the ice-point the pressure could be measured without difficulty to 0.02 millim., the temperature of the dead-space to  $0.01^{\circ}\text{C}.$ ; as has been pointed out in Part I. of this paper, the accuracy of this measurement was of the order of 1 part in 20,000. The errors are thus confined to the measurement of the temperature of the liquid oxygen. In this part of the experiment the pressure could not be measured with certainty to 0.05 millim., though the error certainly never exceeded 0.1 millim., which is equivalent to  $0.03^{\circ}\text{C}.$  Such errors as exist must be attributed to the unequal heating of thermometer bulb, and of the bulb containing the liquid oxygen.

### 7. *The Smaller Constant-Volume Thermometers.*

As has already been stated, the use of a thermometer with a large bulb for the measurement of low temperatures is open to serious objections. In investigating the whole range of vapour pressure of liquid oxygen and of liquid hydrogen, three instruments were used with bulbs of capacities corresponding to 12, 26 and 27 cub. centims. These instruments (fig. 3) did not differ in any important particular from the large thermometer already described, but as it was not necessary to determine the pressure with a degree of accuracy greater than 0.1 millim., the manometer column  $g$ , which was 7 millims. in diameter, was not jacketed with water, and the distance between the surface of the mercury in  $g$  and in the dead-space  $d$  was read directly on a glass scale  $h$ , placed behind the instrument, by means of two telescopes; the readings were corrected to  $0^{\circ}\text{C}.$  The temperature of the dead-space  $d$ , and of the stem as far as  $c$ , was measured by means of a thermometer placed close beside  $d$ . The temperature of the manometer column was taken at the mean between the temperature of the dead-space and the temperature indicated by a thermometer placed at the level of the surface of the mercury in the manometer tube  $g$ .

The thermometer bulb  $d$ , which had a capacity of 12, 26 or 27 cub. centims. in the three thermometers, was sealed to the stem as indicated in the figure, so that if any mercury were accidentally introduced into the bulb, it could be completely removed from it by simply opening the stop-cock  $f$  and lowering the reservoir connected with it.

In making a measurement of temperature by means of a constant-volume gas thermometer, the temperature of the bulb  $a$  and of the dead-space  $d$  are supposed to be constant; and when the latter is measured by means of a mercury thermometer placed beside it, the former can be calculated from the pressure exerted by the gas. The temperature of the vertical portion of the stem  $c$  is, however, uncertain, and is usually taken to be the mean of the extreme temperatures. In measuring very low temperatures, the density of the gas in the dead-space becomes so low that its mass becomes nearly negligible, while the amount of gas in the stem becomes sufficiently

large to make it important to determine its temperature to within a few degrees, particularly when, as in our experiments, it is necessary to employ a small thermometer bulb.

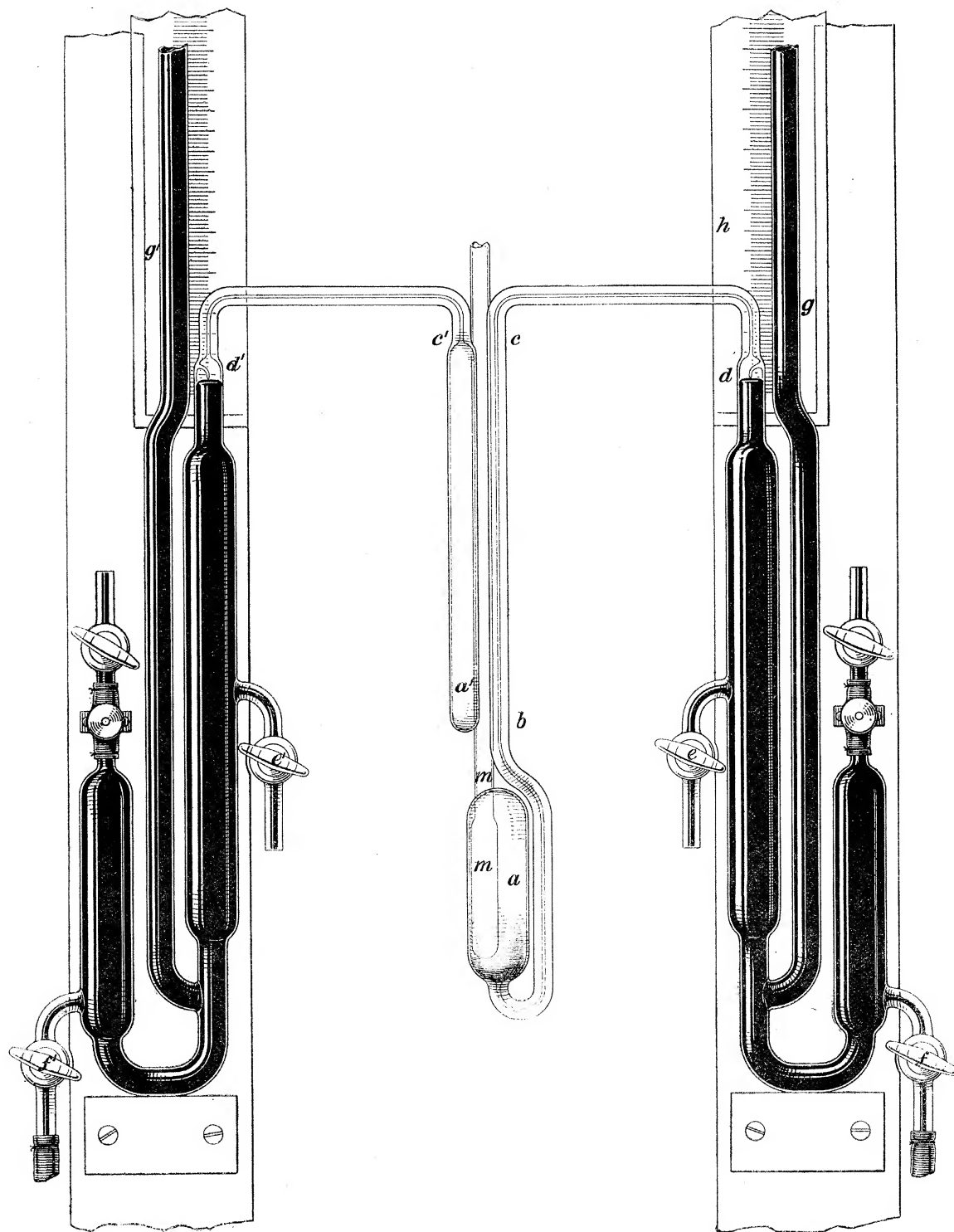


Fig. 3.

To measure the temperature of this portion of the stem we employed the device which is shown in the figure. A second thermometer similar to the one already described, with a cylindrical bulb  $a'$  of the same length as the portion of the stem  $bc$ , was mounted opposite the main thermometer. From the readings of this auxiliary thermometer, taking the temperature of the dead-space and mercury column to be the same in the case of the main thermometer, the mean temperature of the stem could be calculated with sufficient accuracy for our purpose. This device has already been applied by other investigators to similar measurements. The stem of the main and auxiliary thermometers passed at  $c$  through a rubber stopper not shown in the figure. A tube  $nm$ , terminating in a bulb at the lower end, also passed through the rubber stopper, and communicated with a manometer of the type shown in fig. 2, and with an apparatus for generating pure oxygen.

The volume of the bulb and stem to the point  $b$ , of the stem from  $b$  to  $c$ , and of the remainder of the stem and dead-space, were determined by the methods described in Part I. of this paper. As in the previous case, the stem was divided in millimetres between  $b$  and  $c$ .

#### 8. Calibration of the Thermometers.

*Calibration of the stem.*—The volume of one division of the stem was determined before the bulb was sealed to it, by introducing into it a thread of mercury which was measured and subsequently weighed.

*Calibration of the dead-space.*—The volume of the dead-space to the zero point  $C$  on the stem was determined by the method described in Part I. of this paper p. (114). A capillary stop-cock was sealed to the tube which joined the lower part of  $d$ . Mercury was introduced through the stop-cock by means of a rubber tube and mercury reservoir, till it was brought into contact with the point. The stop-cock was then closed, the rubber tube removed, and the mercury run out of the apparatus and weighed. The rubber tube was then re-attached, and, by raising the reservoir, mercury was introduced so as to fill the dead-space and stem to the zero point  $c$  on the scale. This quantity of mercury was weighed as before.

Volumes of the Bulbs.

	A.	B.		C.	
		I.	II.	I.	II.
Weight of bulb filled with water to mark on stem . .	47.5376 (10°·2)	56.3542 (21°·8)	56.3804 (15°·6)	50.0494 (19°·3)	50.0570 (17°·8)
Weight of bulb filled with water to mark on stem . .	35.3322	30.4265	30.4253	23.3048	23.3048
Weight of air in bulb . . .	0.0147	0.0380	0.0280	0.0289	0.0282
Weight of water in bulb . . .	12.2183	25.9557	25.9959	26.7157	26.7233
Volume of bulb . . . . .	12.2217 (10°·2)	26.0110 (21°·8)	26.0075 (15°·6)		
Weight of exp. of glass = 0.000028	12.218	25.9948	25.9959	26.7444	26.7455

### Volumes of the Stems.

Bulb A. 92.5 millims. of stem, 0.2865 gramme of mercury; 1 millim. = 0.00319 gramme  
 103       "       "       0.3300       "       "       1       "       = 0.00320       "  
 1 millim.       "       = 0.000232 cub. centim.  
 Bulb B. 168.8 millims.       "       = 0.65529 millim.  
 1 millim.       "       = 0.000286 cub. centim.  
 Bulb C. The stem was of the same diameter as that of bulb B.

### Volume of the Dead-Space.

Mercury from stop-cock to mark on stem.	Mercury from stop-cock to glass point.	Mercury in dead-space.
Bulb A. 30.6650	26.4225	4.2425
30.6691	26.4225	4.2425
30.6614	26.4225	4.2389
Mean volume of dead-space, 0.313.		
Bulb B. The volume of the dead-space to the mark on the stem was 0.312; it is unnecessary to give further details.		
Bulb C. The volume of the dead-space was the same as in bulb B.		

In calculating the results, the thermometers were considered as divided into three sections.

	A.	B.	C.
The bulb and stem to the level of the bottom of the auxiliary thermometer. Volume . . . . .	cub. centims. 12.216	cub. centims. 25.976	cub. centims. 26.714
The stem for the length corresponding to that of the bulb of the auxiliary thermometer. Volume .	0.035	0.044	0.044
The remaining portion of the stem and dead-space. Volume . . . . .	0.280	0.287	0.287

### The Volume of the Auxiliary Thermometer.

The volume of the bulb and dead-space were determined by the methods already referred to. As great accuracy was not required, details need not be given.

Volume of bulb to *c* (fig. 3) . . . . . 2.124 cub. centims.  
 Volume of dead-space and stem . . . . . 0.204       "

9. *Calculation of the Results.*

The results were calculated by means of the formula :

$$P_0 \left\{ \frac{V + V_s}{273.03} + \frac{V_{ds}}{273 + T_{ds}} \right\} = P \left\{ \frac{V(1 - \alpha(273 - T))}{T} + \frac{V_s}{273 + T_s} + \frac{V_{ds}}{273 + T'_{ds}} \right\},$$

Where  $P_0$  is the pressure on the gas when the bulb and stem were immersed in ice,

$P$  is the pressure on the gas when the bulb is at the temperature to be measured,

$V$  is the volume of the bulb at  $0^\circ \text{C}$ .,

$V_s$  is the volume of the stem from B to C,

$V_{ds}$  is the volume of the dead-space,

$\alpha$  is the coefficient of expansion of the glass,

273.03 is the melting-point of ice on the gas scale, the reciprocal of the pressure coefficient of the gas with which the thermometer is filled,

$T$  is the temperature to be measured,

$T_{ds}$  and  $T'_{ds}$  are the temperatures of the dead-space in degrees Centigrade,

$T_s$  is the temperature of the stem calculated from the readings of the auxiliary thermometer.

In calculating  $T_s$ , the following formula was employed :

$$P_0 \left\{ \frac{V}{273} + \frac{V_{ds}}{273 + T_{ds}} \right\} = P \left\{ \frac{V}{T_s} + \frac{V_{ds}}{273 + T'_{ds}} \right\}.$$

Since for each series of observations the ice-point remained constant, the left-hand side of each equation could be expressed by a constant for each filling of the thermometer.

10. *Vapour Pressures of Liquid Oxygen on the Constant-Volume Hydrogen Scale.*

(I.) March, 1901. Thermometer A (12 cub. centims. bulb).

## Ice-Point of Thermometer.

Pressure on gas (corr.).	Temperature of dead- space.	Constant.
millims. 844.65	$^\circ \text{C}$ . 15.30	38.7114

The constant for the auxiliary thermometer was in this experiment determined by measuring the pressure when the bulb and dead-space were at the same temperature

Pressure on gas.	Temperature of bulb and dead-space.	Constant.
millims. 824·3	° C. 18·0	6·59

### Vapour Pressures of Liquid Oxygen.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid oxygen.	Temperature	
				Found.	Calculated.
millims.	° C.	° H. scale.	millims.	° H. scale.	° H. scale.
266·9	16·60	132	411·3	84·60	84·62
267·25	16·80	132	416·6	84·70	84·73
267·80	16·80	134	424·6	84·86	84·88
268·30	16·82	136	430·5	85·04	84·99
268·40	16·83	136	432·6	85·07	85·04
269·10	17·00	139	443·8	85·20	85·26

(II.) Thermometer A, refilled with hydrogen.

Ice-Point, March 19th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
	millims.	° C.	
Main thermometer . . . .	974·1	15·9	44·651
Auxiliary thermometer . . .	887·5	15·0	7·53

## Vapour Pressures of Liquid Oxygen.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid oxygen.	Temperature	
				Found.	Calculated.
millims.	° C.	° H. scale.	millims.	° H. scale.	° H. scale.
(a) March, 20th, 1902.					
323·0	16·6	140	664·2	88·79	88·84
323·5	16·6	142	668·9	88·93	88·92
325·2	16·8	149	703·6	89·39	89·38
325·5	16·8	152	708·3	89·48	89·44
(b) March 21st, 1902.					
293·95	16·6	136	252·1	80·78	80·77
294·45	16·7	141	258·4	80·91	80·95
294·85	16·8	146	260·3	81·02	81·03
(c) March 24th, 1902.					
303·7	12·9	119	356·7	83·44	83·46
304·0	13·1	121	359·4	83·52	83·52
304·4	13·3	125	364·7	83·63	83·64
309·3	14·1	158	427·2	85·01	84·98
309·45	14·2	159	429·4		
309·7	14·3	159	432·5		
(d) March 25th, 1902 (Morning).					
301·7	14·6	143	330·1	82·75	82·75
301·1	14·6		324·9		
301·2	14·7		325·4		
(e) March 25th, 1902 (Afternoon).					
309·7	13·4	121	434·5	85·18	85·19
309·9			438·4		
310·15			445·4		

In this set of experiments a little mercury was accidentally introduced into the bulb of the auxiliary thermometer, which was taken as being somewhat shorter and of smaller capacity.

(III.) Thermometer B (26 cub. centims. bulb), filled with hydrogen, June 2nd.

Ice-Point of Thermometer.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 952·55	° C 17·75	91·717
Auxiliary thermometer . . .	954	17·75	8·093

Vapour Pressure of Liquid Oxygen.

June 3rd, 1902.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressure of liquid oxygen.	Temperature	
				Found.	Calculated.
millims. 293·75	° C. 19·1	° H. scale. 98	millims. 346·7	° H. scale. 83·24	° H. scale. 83·23

This result is the mean of two very concordant observations.

11. *The Vapour Pressures of Liquid Oxygen on the Constant-Volume Helium Scale.*

(I.) Thermometer A (12 cub. centims. bulb).

The helium, which had been obtained by heating clèveite, was purified by sparking with oxygen, and was afterwards passed through liquid oxygen condensed in a bulb and cooled to below  $-200^{\circ}$  C. The gas was passed through a bulb immersed in liquid air on its way into the thermometer.

Ice-Point of the Thermometer.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 966·9	° C. 14·6	44·327

The auxiliary thermometer was still filled with hydrogen.



## Vapour Pressure of Liquid Oxygen.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid oxygen.	Temperature	
				Found.	Calculated.
millims.	° C.	° He. scale.	millims.	° He. scale.	° He. scale.
(a) March 13th, 1902.					
324·5	18·2	199	764·0	90·36	90·25
326·45	18·3	208	685·5	89·22	89·22
(b) March 17th, 1902.					
322·9	17·8	165	677·5	89·10	89·12
323·2	17·8	169	682·1	89·18	89·18
323·5	18·0	176	686·7	89·27	89·25
323·6	18·0	180	688·2	89·29	89·28

## (II.) Thermometer A.

The thermometers were filled with helium purified by passing it through a coil immersed in liquid hydrogen at its boiling-point (Appendix III.).

## Ice-Point of Thermometers, April 17th and March 25th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
	millims.	° C.	
Main thermometer { March 25th . . . . .	976·94	18·9	44·769
{ April 17th . . . . .	976·42	15·5	44·756
Auxiliary thermometer . . . . .	996	16	7·73

## Vapour Pressure of Liquid Oxygen.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid oxygen.	Temperature	
				Found.	Calculated.
millims.	° C.	° He. scale.	millims.	° He. scale.	° He. scale.
324·75	20·0	175	675·5	89·10	89·09
324·75	20·4	167	677·0	88·96	89·13

## (III.) Thermometer B (26 cub. centims. bulb).

The thermometers were filled with helium purified by passing it through a coil cooled to  $15^{\circ}5$  by means of liquid hydrogen boiling under reduced pressure (Appendix III.).

## Ice-Point of Thermometer, June 4th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 939.95	$^{\circ}$ C. 17.35	90.503
Auxiliary thermometer. . .	954	17.3	8.093

## Vapour Pressure of Liquid Oxygen

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid oxygen.	Temperature	
				Found.	Calculated.
millims. 288.1 288.7	$^{\circ}$ C. 17.7 18.0	$^{\circ}$ He. scale. 98 100	millims. 322.0 328.0	$^{\circ}$ He. scale. 82.73 82.90	$^{\circ}$ He. scale. 82.74 82.89

## (IV.) Thermometer C (26.7 cub. centims. bulb).

The helium was from the same sample as was used in the last experiment.

## Ice-Point of Thermometer, June 11th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 922.25	$^{\circ}$ C. 16.90	91.204

The auxiliary thermometer was not refilled.

## Vapour Pressure of Liquid Oxygen.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid oxygen.	Temperature	
				Found.	Calculated.
millims.	° C.	° He. scale.	millims.	° He. scale.	° He. scale.
*307·70	16·0	103	750·5	90·11	90·08
†307·94	16·5	105	755·5	90·18	90·15
305·00	17·1	98	692·0	89·32	89·32
300·45	17·1	98	600·5	87·99	88·02
291·95	17·0	89	449·0	85·47	85·46
301·05	17·0	97	608·5	88·17	88·15
292·30	16·8	78	456·0	85·58	85·58

In this experiment the vacuum vessel surrounding the thermometer bulb, &c., was first of all filled with nearly pure liquid oxygen. The liquid was made to boil steadily by passing a current of gaseous oxygen into the liquid. Liquid air was added to the liquid oxygen to obtain the lower temperature. Between the first and second observations the manometer and bulb containing the pure oxygen were exhausted and refilled.

12. *Treatment of the Results.*

The figures given in the last column of the foregoing tables are the temperatures, corresponding to the observed pressures, taken from the smoothed vapour pressure curves shown in Plate 1. It will be observed that the points obtained by direct observation lie in every case very close to the curve, and that the difference between the observed and calculated temperatures rarely exceeds two or three hundredths of a degree.

The results obtained by direct observation of the vapour pressures were smoothed by the method of RAMSAY and YOUNG ('Phil. Mag.', 1886, vol. 21, p. 33; vol. 22, p. 37). This method consists in calculating the ratios of the absolute temperatures  $T_a$ ,  $T_b$ ,  $T'_a$ ,  $T'_b$ , &c., for any pair of substances A and B corresponding to vapour pressures  $p$ ,  $p'$ , &c., and plotting the ratios  $T_a/T_b$ ,  $T'_a/T'_b$ , &c., against the temperature  $T_a$ ,  $T'_a$ , as rectangular coordinates. The points so defined lie on a straight line, from which the temperature corresponding to any pressure  $p$  for the substance B can be calculated, by first finding the temperature  $T_a$  corresponding to that vapour pressure for the substance A, determining the value of the ratio  $T_a/T_b$ , and dividing the value of  $T_a$  by it. In smoothing our results we took water as the second substance A.

Two sets of ratios were obtained by this method, corresponding to the tempera-

\* The mean of two observations.

† The mean of four observations.

tures of liquid oxygen on the hydrogen and helium scales. When the results were plotted against the absolute temperatures of water two parallel straight lines were obtained. From these lines the smoothed values of the ratios corresponding to those temperatures at which the vapour pressures of water have the values expressed in the following table were determined, and from them the corresponding temperatures of liquid oxygen on the scale of the two thermometers were calculated (see Plate 1).

### 13. *The Vapour Pressures of Liquid Oxygen.*

Pressures in millimetres of mercury.	Temperatures on the hydrogen scale.	Temperatures on the helium scale.
800	90·60	90·70
790	90·47	90·57
780	90·35	90·45
770	90·23	90·33
760	90·10	90·20
750	89·97	90·07
740	89·85	89·95
730	89·71	89·81
720	89·58	89·68
710	89·46	89·56
700	89·33	89·43
650	88·65	88·75
600	87·91	88·01
550	87·13	87·23
500	86·29	86·39
450	85·37	85·47
400	84·39	84·49
350	83·31	83·41
300	82·09	82·19
250	80·70	80·80
200	79·07	79·17
150	77·07	77·17

### 14. *Discussion of the Results.*

When the results which are tabulated in the preceeding table are plotted on a diagram, it will be observed that the vapour pressures of liquid oxygen on the scale of the two thermometers are expressed by two curves, and that the temperature corresponding to any particular pressure is always 0·1° higher on the helium scale than on the hydrogen scale. As we shall show later (Part III., p. 169), the divergence becomes still greater at lower temperatures.

Though the pressure coefficients for hydrogen and helium between the melting-point of ice and the boiling-point of water do not appear to differ appreciably, and though at the normal temperature these gases may be considered as nearly perfect, it

is not surprising that they exhibit a difference at lower temperatures. It must be remembered that while the critical point of hydrogen is about  $35^{\circ}$  abs., it is probable (Part III., p. 177) that the critical point of helium does not lie far from  $10^{\circ}$  abs. The temperature of liquid air, about  $85^{\circ}$  abs., expressed as a multiple of critical temperature of the gas, is 8 with regard to helium, and 2.5 with regard to hydrogen, which is at that temperature in a state corresponding to that of oxygen, of which the critical point is  $150^{\circ}$  abs., at the boiling point of water. At this temperature we have no reason to believe that oxygen behaves in any way as a perfect gas.

Further, as was first shown by WROBLEWSKI (*loc. cit.*, p. 136), and later by two of us (TRAVERS and SENTER, 'Brit. Assoc.' 1901), the coefficient of expansion of hydrogen at constant pressure between the normal temperature and the temperature of liquid air increases rapidly with rise of pressure. This tends to confirm the result which we now bring forward, *that at an initial pressure of 1 metre of mercury at the melting-point of ice, the constant volume hydrogen and helium scales differ by 0.1 at the boiling-point of liquid oxygen.* At lower initial pressures the difference between the two scales of temperature might possibly be smaller.

### 15. *The Probable Accuracy of the Results.*

It may at once be pointed out that in experiments of this kind the probable accuracy cannot be arrived at by any method of calculation. So far as the actual measurements of temperatures and pressures are concerned, they may easily be made to 1 in 10,000. In discussing the actual experiments we have, however, to consider such sources of error as may be due to the superheating of the liquid of which the vapour pressure is being determined; inequalities in the temperature of the liquid in which the thermometer was immersed; and errors due to impurities in the gases and liquids employed.

It will be observed that in the course of our work we have employed four different thermometers, the large thermometer used for determining the pressure coefficients of the gases between  $0^{\circ}$  and  $100^{\circ}$  C., and three smaller instruments of which the bulbs had capacities of 12 cub. centims. (A), 26 cub. centims. (B), and 26.7 cub. centims. (C), respectively. Though the large thermometer should give the most accurate results, and, indeed, differentiation of the equations employed in calculating the results indicates that the errors of measurement of a steady temperature of about  $85^{\circ}$  abs. should be accurate to 0.005, it appears to be impossible to maintain so large a thermometer bulb at a uniform and steady temperature. We have therefore considered that the results obtained by means of the smaller thermometers, which are very concordant among themselves, and differ only by  $0.1^{\circ}$  from the results obtained by means of the large thermometer, are the most accurate. The values of the boiling-point and vapour pressures of liquid hydrogen determined by means of

the same thermometers show an even closer agreement ; this, as we shall presently show, is due to the fact that liquid hydrogen, unlike liquid oxygen, does not tend to become superheated.

It is a somewhat remarkable fact that pure oxygen when liquified can only with difficulty be made to boil steadily. By passing a rapid current of oxygen or air through the liquid a fairly steady temperature may be maintained, but if the current is stopped the temperature may rise more than one degree. This probably accounts for the fact that the temperatures found by us are in every case somewhat lower than those of other observers, who, without exception, measured the pressure on the mass of liquid in which the thermometer was immersed. This source of error we have, however, taken great pains to eliminate ; for the accuracy of the actual measurements, the concordance of the observation made by means of the different thermometers furnishes a sufficient guarantee.

## PART III.

*On the Vapour Pressures of Liquid Hydrogen at Temperatures below its Boiling-Point on the Constant-Volume Hydrogen and Helium Scales.*

*By* MORRIS W. TRAVERS, *D.Sc., Fellow of University College, London,*  
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1. *Previous Investigations.*

THE boiling-point of liquid hydrogen has been measured directly by DEWAR and indirectly by OLSZEWSKI. The former employed constant-volume hydrogen and helium thermometers, the latter, however, containing a mixture of helium and neon, obtained by a method which will be discussed later (p. 171). The results are as follows ('Roy. Soc. Proc.' Feb. 1901, vol. 68, p. 40):—

	Pressure of the gas in thermometer at 0° C.	Temperature of liquid hydrogen.	Atmospheric pressure.
	millims.	° C.	millims.
Hydrogen thermometer (a) . . . . .	286·6	– 253·03	760·6
„ „ (b) . . . . .	269·8	– 253·37	764·4
„ „ (c) . . . . .	127·0	– 250·35	759·5
„ „ (d) . . . . .	739·0	– 252·81	770·5
Helium thermometer (a) . . . . .	728·0	– 252·68	765·0
„ „ (b) . . . . .	728·0	– 252·84	770·0

The boiling-point of liquid oxygen was measured in every case as a check on the results.

The results obtained by means of the hydrogen thermometer filled under a pressure of 739 millims. of mercury differ from the mean of our observations by  $0^{\circ}\cdot 1$ . The difference between this result and those obtained in experiments (*a*), (*b*) and (*c*) is certainly due to experimental error, since the temperatures determined by means of a gas thermometer should rise when the pressure on the gas in the thermometer is reduced. Since the pressure on the gas in the thermometer was in each of these experiments very small, the experimental error was proportionally large, and much greater weight must be attached to the last measurement.

The results obtained by means of the helium thermometer are lower than those obtained by us, though the difference is not constant.

Pressure.	Temperature.		
	DEWAR.	T. and J.	$\Delta$ .
	$^{\circ}\text{C.}$		
770	$-252^{\circ}\cdot 84$	$-252^{\circ}\cdot 57$	$0^{\circ}\cdot 27$
765	$-252^{\circ}\cdot 68$	$-252^{\circ}\cdot 60$	$0^{\circ}\cdot 08$

OLSZEWSKI ('Phil. Mag.,' 1895 (5), vol. 39, p. 199; vol. 40, p. 202) employed the following method: Hydrogen was compressed to 170 atmospheres into a steel cylinder, with a loose glass lining enclosing the platinum coil of a resistance thermometer, of which the resistance had been determined at  $0^{\circ}$ ,  $-78^{\circ}$ ,  $-182^{\circ}\cdot 5$  and  $-208^{\circ}\text{C.}$  The cylinder was cooled in liquid air, boiling *in vacuo*, and the gas was then allowed to escape from the cylinder. When the pressure fell to one atmosphere the resistance of the coil was measured, and the temperature determined by linear extrapolation. As the result of numerous trials, he found the temperature to be  $-243^{\circ}\cdot 5$ .

Though the method gave accurate results for the boiling-point of oxygen, the results are of no value so far as the temperature of liquid hydrogen is concerned, as the variation of the resistance of platinum with the temperature is not linear.

Beyond determining the boiling-point of liquid hydrogen on the scales of the two thermometers, DEWAR ('Roy. Soc. Proc.,' vol. 68, p. 360) finds the melting-point on the helium scale to be  $16^{\circ}$ ; an earlier determination by him gives the melting pressure as 55 millims. (T. and J. find  $14^{\circ}\cdot 1$  and 49 millims. respectively, p. 170.) He also gives the following values for the temperatures of solid hydrogen corresponding to very low pressures (*loc. cit.*):—



	Thermometer 2.	Thermometer 3.
Vapour pressures . . .	764·4 millims., 30–40 millims.	759·5 millims., 30–40 millims.
Temperatures . . .	– 253·37° C., – 258·66° C.	– 250·35° C., – 255·67° C.

As has already been pointed out (p. 156), the pressure on the gas in these thermometers was very small, and little weight can be attached to the results.

## 2. *The Liquefaction of Hydrogen.*

The liquid hydrogen employed in these researches was obtained by means of an apparatus devised and constructed by one of us two years ago. The apparatus as it was originally designed, has been described in the 'Philosophical Magazine' (1901, vol. 17, 411), and such slight modifications as have since been introduced are referred to in the treatise, TRAVERS on 'The Experimental Study of Gases,' p. 206. The hydrogen was obtained by the action of dilute sulphuric acid upon commercial granulated zinc, contained in a cylindrical lead vessel, of which the joints had been soldered in the oxyhydrogen blow-pipe. The gas was purified by passing it first through a solution of potassium permanganate; through two glass towers, each  $1\frac{1}{2}$ -metres in length, containing broken pumice over which a sulphuric acid solution of potassium bichromate ran continuously; through a third glass tower containing pumice kept moist with silver nitrate solution; and finally, through a wash bottle containing caustic potash solution, into the gasometer. In this way it was possible to obtain hydrogen from which but little solid separated during the process of liquefaction.\*

In one experiment in which we failed to obtain liquid hydrogen, owing to the formation of solid air in the vacuum vessel enclosing the regenerator coil, we found that the packing of the low-pressure piston of the compressor had become so worn that air was being taken into the cylinder with the hydrogen. With compressors of the "Whitehead" type, in which the piston-rod does not pass through a gland, and the compression is only affected by the inward motion of the piston, special care must be taken that the piston packing or cup-fibre fits the cylinder.

In connection with the work on liquid hydrogen, we wish to express our thanks to Mr. HOLDING, Mechanic in the Chemical Department of University College, for his invaluable services.

\* In connection with the preparation of the hydrogen, a curious observation was made which has not been explained. The silver nitrate solution which escaped at the bottom of the tower appeared almost immediately to deposit pure silver in the form of small bright metallic crystals. Very little silver appeared to form inside the tower, and it seems as if some compound were produced which decomposed in contact with the air. The hydrogen had already passed through two towers containing acid chromate solution, and it is possible that hydrogen, like oxygen, becomes more active when it takes part in a slow chemical reaction.

### 3. *The Manipulation of Liquid Hydrogen.*

In each experiment we employed about 400 centims. of liquid hydrogen, which, when sufficient liquid air (about 8 litres) had been accumulated to cool the apparatus, could be obtained in less than 1 hour from the time of commencing the operations.

Though perhaps it is little to be expected, it is a fact that it is much easier to make measurements of the boiling-point and vapour pressures of liquid hydrogen than of liquid oxygen. As we have already stated (p. 140), liquid air tends to become superheated, and only with difficulty can it be made to boil steadily. Liquid hydrogen, on the other hand, can be made to boil quite steadily at any temperature between its boiling-point and melting-point. Possibly this may be due to the presence of finely divided particles of solid air suspended in it, for it does not appear that the phenomenon of superheating is dependent upon any intrinsic property of a liquid.

That the value of the latent heat of vaporisation is very high (DEWAR, 'Roy. Soc. Proc.,' June 13th, 1901, vol. 68, 361) is also in favour of the experimenter; for as the boiling-point of hydrogen is more than sixty degrees lower than the temperature of liquid air, the operation of cooling a thermometer bulb, previously cooled in liquid air, to the boiling-point of liquid hydrogen, necessitates the absorption of a considerable quantity of heat.

When the vacuum vessel which received the liquid hydrogen from the liquefier was filled with the liquid it was at once removed from the apparatus, plugged with animal wool, and enclosed in an outer vessel containing liquid air. The mouth of a vessel containing liquid hydrogen cannot be left open, as in that case air enters the vessel, solidifies, and rapidly evaporates the liquid. A plug of natural wool is preferable to a cork or rubber stopper, for the interstices of wool become filled with cold vapour, and the plug acts as an excellent insulator, whereas the heat radiated from the solid stopper helps to evaporate the liquid.

### 4. *Method of Determining the Vapour Pressures of Liquid Hydrogen.*

The thermometers employed in these researches were identical with those used in determining the vapour pressures of liquid oxygen, and in nearly every case in which a measurement was made with liquid hydrogen, a point on the vapour-pressure curve of oxygen was also determined as a check upon the results. The apparatus as arranged for these experiments is shown in section in fig. 1. The thermometer has already been fully described in Part II. of this investigation, so that to simplify the description only the bulb  $\alpha$  of the main thermometer, and the bulb  $\alpha'$  of the auxiliary thermometer, by means of which the temperature of the stem of the main thermometer was determined, are shown in the present diagram.

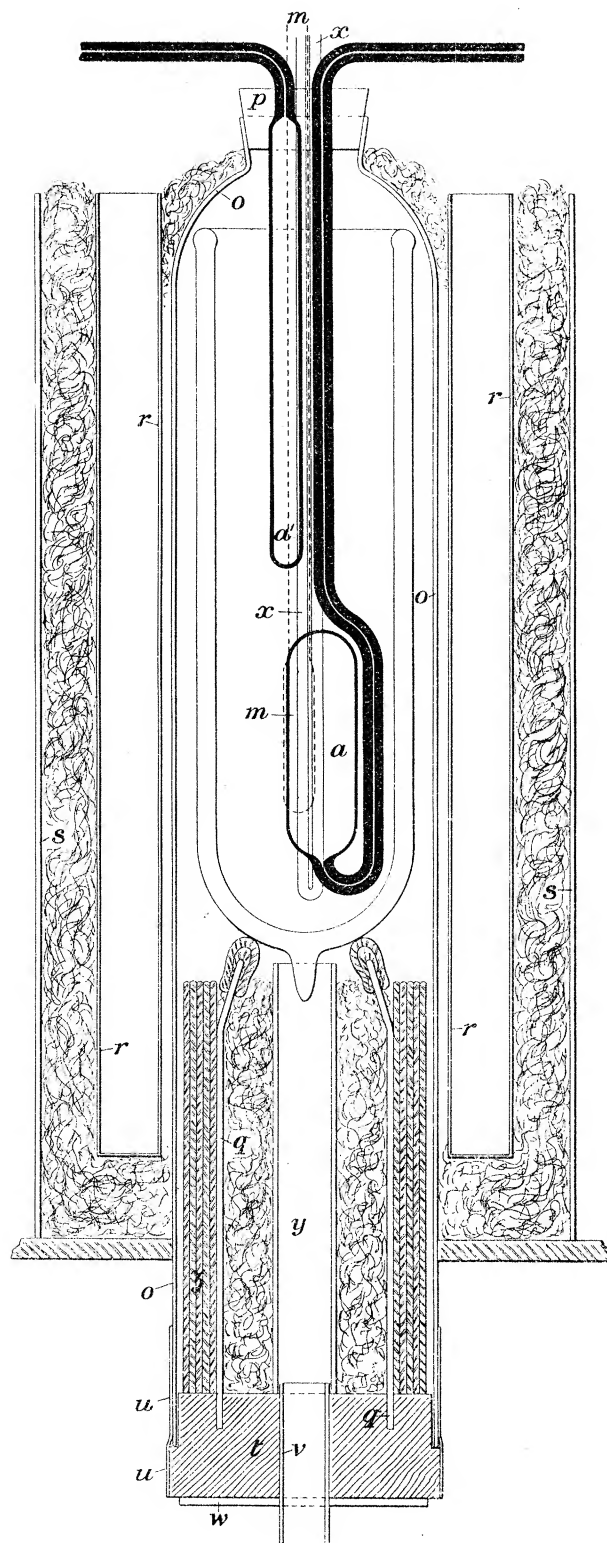


Fig. 1.

The stem of the main and auxiliary thermometers passed through two holes in a rubber stopper, *p*. Through one of two holes, pierced at right angles to the first, passed the stem of the bulb which contained pure hydrogen (pp. 138, 139) and communicated with a manometer. The capillary tube, *x*, which was sealed at its lower end, communicated with a compression apparatus containing helium, passed through the other hole. This tube was employed in an attempt to liquefy helium, which will be dealt with later. In order to make the diagram clearer, the glass walls and stem of the thermometer are blacked in, the compression tube is drawn in outline, and the tube and bulb for the pure liquid hydrogen is represented by the dotted line.

The thermometer bulb, &c., was enclosed within a wide glass tube, *o*, 75 millims. in diameter and 400 millims. long. This tube was open at the bottom for the introduction of the vacuum vessel containing the liquid hydrogen, and at the top was formed into a neck to fit the rubber stopper, *p*. Surrounding this tube for a considerable part of its length was an annular zinc vessel, open at the top, which could be filled with liquid air. This vessel was in turn surrounded with natural wool enclosed within a jacket of linoleum. The diameter of the linoleum jacket was such that it exactly filled the space between the vertical wooden supports to which the main and auxiliary thermometers were fixed (p. 141). The liquid-air jacket was not essential to the working of the apparatus, even when the liquid hydrogen in the vacuum vessel was boiling under reduced pressure at the extremely low temperature of  $14^{\circ}$  abs. It was thought that by using it an economy in the liquid hydrogen would be effected, but it is impossible to determine whether this was actually the case. Wool was packed into the top of the tube, *o*, and between the tubes which projected downwards through the rubber stopper, to shield off radiation from above.

The vacuum vessel containing the liquid was inserted from the lower and open end of the tube, *o*, so as to surround the thermometer bulb, and was kept in place by the arrangement shown in the figure. A stopper, *t*, made of boxwood, was turned on the lathe to fit the open end of the tube, *o*, and an air-tight junction between the two was made by means of a rubber sleeve, *u*. The sleeve was fixed permanently to the stopper, and the upper part of it could be rolled back, and then slipped over the tube, *o*, when the stopper was in position. A brass tube, *v*, passing through the stopper, could be connected with the exhaust pump by means of a rubber connection and lead tube; as the brass tube was soldered to a heavy brass plate, *w*, which was screwed to the outer surface of the stopper, it never became cold, and a good junction with the rubber tube was maintained during the experiment. It may be remarked here that in carrying out experiments at low temperatures, it is impossible to make air-tight junctions between frozen rubber and metal on account of the greater contraction of the latter.

The vacuum vessel was supported on four wires, *qq*, let into the wooden stopper and covered at the top with pads of cloth. Wire rings were soldered to them at

intervals, and round the cage so formed baize,  $z$ , was wound to form a plug a little smaller than the inner diameter of the tube,  $o$ . A glass tube,  $y$ , served as a continuation of the tube,  $v$ , and the space between  $y$  and  $z$  was packed with animal wool. By means of this plug the vacuum vessel was effectually shielded from radiation from below.

The method of filling the thermometer bulb has already been dealt with in a previous section of the work (p. 117). The ice point of the thermometer was of course determined before the tube,  $o$ , was placed in position.

Before commencing an experiment with liquid hydrogen a vacuum vessel containing liquid air was first introduced into the tube,  $o$ , and temporarily held in position by means of the plug; in this manner the bulb of the thermometer was cooled down to  $-185^{\circ}\text{C}$ . When the vessel containing the liquid air was again lowered, the wool was removed from the mouth of the vacuum vessel containing the hydrogen, which was brought below the apparatus, and slowly raised into position by means of the plug. The rubber sleeve,  $u$ , was then turned upwards over the tube,  $o$ , and secured in position by means of a piece of wire.

The actual measurement of the vapour pressure was made in the same manner as has been described in the case of oxygen (p. 138). One observer read the pressures indicated by the manometer connected with the tube,  $m$ , in which pure hydrogen was liquefied, while the other took simultaneous readings of the main thermometer, of the auxiliary thermometer, and of the temperature of the dead space. So steadily did the hydrogen boil under normal pressure that this operation could be carried out without the least difficulty. It is noticeable that the vapour pressure of the pure hydrogen in the bulb,  $m$ , was always slightly higher than the barometric pressure. This is to be attributed to the presence of small quantities of impurities dissolved in the main quantity of hydrogen in the vacuum vessel, and confirms our reasons for adopting this method of measuring the vapour pressures.

In determining the vapour pressure of liquid hydrogen at lower pressure we employed the following method: The tube,  $v$ , was connected by a short rubber tube to a wide lead tube which communicated with the exhaust pump, with a large glass globe 300 millims. in diameter, with a mercury manometer, and with a fine adjustment stopcock, through which air could be admitted to the apparatus and the pressure so regulated.

The exhaust was maintained by means of a large two-cylinder 'Fleuss' pump, worked by a one horse-power electric motor. This pump, which was also used in connection with the apparatus for producing liquid hydrogen, was arranged so that the two cylinders could be worked in parallel to give a vacuum of 50 millims. of mercury, or in series to give a vacuum of less than 1 millim. of mercury. For reasons which will be entered into presently we have confined our measurements to pressure above 50 millims. of mercury. By opening and closing the fine adjustment cock, so as to admit more or less air into the apparatus, the pressure could be maintained

steady for a length of time amply sufficient for the equalisation of temperature throughout that part of the apparatus which was enclosed within the vacuum vessel.

### 5. *Calculation of the Results.*

The method of calculating the temperatures of liquid hydrogen was the same as has been described in Part II. of this work. It may be pointed out here that, at very low temperatures, the mass of gas in the stem of the thermometer becomes considerable, while the mass of gas in the dead space becomes nearly negligible. Taking a specific case :—

Constant for thermometer . . . . .	44·769
Pressure of gas in thermometer . . . . .	55·0 millims.
Volume of bulb . . . . .	12·187
„ „ stem . . . . .	0·035
„ „ dead-space . . . . .	0·280
Temperature of stem . . . . .	30° abs.
„ „ dead-space . . . . .	288° „

The equation for determining the temperature  $T$  now becomes :—

$$44\cdot769 = 55\cdot0 \left\{ \frac{12\cdot187}{T} + \frac{0\cdot035}{30} + \frac{0\cdot280}{288} \right\},$$

where the second term within the bracket is equal to 0·0012, and the third term is less than 0·001. In both cases the correction is exceedingly small.

In calculating the volume of the bulb, the coefficient of expansion of glass between 0° and 253° C. was taken as 0·000019 for the following reasons :—The coefficient of expansion between 0° and 100° C. is 0·0000285, between 0° and — 185° it is 0·0000218; on extrapolation one obtains the value which we have taken for the coefficient. The following values for the volume of the bulb at — 253 are calculated for different coefficients :—

Coefficient.	Volume.
0·000019	25·850
0·000021	25·837

This difference of volume corresponds to a difference of 0·01 in the boiling-point of hydrogen.

6. *The Vapour Pressures of Liquid Hydrogen on the Constant-Volume Hydrogen Scale.*

(I.) Thermometer A (12 cub. centims. bulb).

Ice-Point of Thermometer, May 7th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 953·05	° C. 15·85	43·679

The auxiliary thermometer was already filled with helium (Part II., § 11, II.), it was not refilled with hydrogen, for when the bulb of the main thermometer was cooled in liquid hydrogen boiling under reduced pressure, hydrogen might condense in the bottom of the bulb of the auxiliary thermometer.

Vapour Pressures of Liquid Hydrogen.

May 28th, 1902.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of hydrogen.	Temperature	
				Found.	Calculated.
millims.	° C.	° He. scale.	millims.	° H. scale.	° H. scale.
72·04	18·3	40	757·2	20·17	20·21
66·35	18·6	51	458·6	18·57	18·56
62·40	18·6	50	309·0	17·45	17·44
62·80	18·6	45	321·8	17·56	17·55
58·40	18·8	56	198·0	16·33	16·35

(II.) Thermometer B (26 cub. centims. bulb).

Ice-Point of Thermometer, June 4th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 952·55	° C. 17·55	91·930
Auxiliary thermometer. . .	954	17·55	8·093

## Vapour Pressures of Liquid Hydrogen.

June 4th, 1902.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid hydrogen.	Temperature	
				Found.	Calculated.
millims.	° C.	° H. scale.	millims.	° H. scale.	° H. scale.
71·83	18·1	27	766·6	20·28	20·25
71·83	18·2	29	766·6		

For the vapour pressure of liquid oxygen on this thermometer, see Part II., 10 (III.).

*7. The Vapour Pressures of Liquid Hydrogen on the Constant-Volume Helium Scale.*

(I.) Thermometer A (12 cub. centims. bulb). For preparation of helium (fraction 1), see pp. 172, 174.

Ice-Point of Thermometer, April 17th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 976·42	° C. 16·0	44·760
Auxiliary thermometer . . .	996·5	18·9	7·73



## Vapour Pressures of Liquid Hydrogen.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressure of liquid hydrogen.	Temperature	
				Found.	Calculated.
millims.	° C.	° He. scale.	millims.	° He. scale.	° He. scale.
April 18th, 1902.					
74·83	15·5	31	765·0	20·42	20·44
72·09	15·2	29	604·1	19·70	19·63
72·04	14·9	28	606·6	19·69	19·61
67·26	14·6	26	390·5	18·38	18·28
55·98	14·3	21	100·0	15·29	15·14
55·48	14·0	25	98·0	15·15	15·10
55·43	13·7	25	97·5	15·14	15·09
May 1st, 1902.					
74·75	15·6	41	759·2	20·41	20·41
68·70	15·3	33	449·0	18·76	18·70
55·20	15·2	27	96·8	15·07	15·08
55·30	15·2	27	75·8	14·55	14·67
52·90	15·1	27	69·4	14·44	—
52·20	15·1	27	62·0	14·25	14·38
55·05	14·8	35	95·3	15·01	15·06
51·30	14·7	31	55·2	14·00	14·22
55·00	14·7	91	95·6	15·01	15·05
51·90	15·0	29	59·2	14·16	14·32

For measurement of vapour pressures of liquid oxygen with this thermometer, see Part II., 11 (II.).

(II.) Thermometer B (26 cub. centims. bulb). Helium purified by passing through a coil cooled to 15°·5 abs. (see p. 174).

## Ice-Point of Thermometer, June 4th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 939·95	° C. 17·35	90·516
Auxiliary thermometer . . .	954·0	17·35	8·093

## Vapour Pressures of Liquid Hydrogen.

June 13th, 1902.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid hydrogen.	Temperature	
				Found.	Calculated.
millims. 71·45	° C. 20·0	° He. 58	millims. 770·0	° He. 20·43	° He. 20·46

This result is the mean of two consecutive observations, which were nearly identical. The quantity of pure liquid hydrogen in the vapour pressure bulb (*m*, fig. 1) was increased between the two readings.

For the measurements of the vapour pressure of liquid oxygen with this thermometer, see Part II., 11 (III.).

III. Thermometer C (26·7 cub. centims. bulb). The thermometer was filled with helium from the same sample as was used in the last series of experiments.

## Ice-Point of Thermometer, June 11th, 1902.

	Pressure on gas in thermometer.	Temperature of dead-space.	Constant.
Main thermometer . . . .	millims. 924·25	° C. 16·9	91·505
Auxiliary thermometer. . .	954·0	17·3	8·093

## Vapour Pressures of Liquid Hydrogen.

June 12th, 1902.

Pressure on gas in thermometer.	Temperature of dead-space.	Temperature of stem.	Vapour pressures of liquid hydrogen.	Temperature	
				Found.	Calculated.
millims.	° C.	° He.	millims.	° He.	° He.
*69·79	15·4	28	749·0	20·36	20·36
†55·45	16·1	26	169·2	16·17	16·19
†51·70	16·3	25	96·2	15·08	15·07
†50·95	16·4	24	83·0	14·86	14·82
†50·80	16·6	26	80·2	14·81	14·76
†50·55	16·6	30	76·3	14·74	14·70
53·70	16·4	33	129·8	15·65	15·63

For the measurement of the vapour pressures of liquid oxygen, with this thermometer, see Part II., 11 (IV.).

8. *Treatment of the Results.—Their Probable Accuracy.*

As we shall presently find, the melting point of hydrogen is 14·1 on the helium scale, and consequently the whole of the observations recorded in the foregoing tables refer to liquid hydrogen only. As in the case of liquid oxygen (Part II., p. 151), the experimental results were smoothed by the method of RAMSAY and YOUNG, and the vapour-pressure curves for liquid hydrogen on the scales of the hydrogen and helium thermometers were plotted on a diagram as in Plate 1. The last columns of the preceding tables contain the temperatures read off the curves at points corresponding to the observed pressures.

It will be observed that at pressures near 760 millims. the points representing actual observation lie either on, or very close to, the curve. Of these points there are four on the curve representing the vapour pressures on the helium scale, obtained by means of three separate thermometers; there are two similar points on the curve representing the vapour pressures on the hydrogen scale, the results of observations with two different thermometers. We can therefore consider that the boiling-point of liquid hydrogen, which is 20°·22 on the hydrogen scale and 20°·41 on the helium scale, has been determined with a high degree of accuracy.

\* The mean of two nearly coincident observations.

† In these observations the vapour pressures of hydrogen were measured on two manometers, connected with two bulbs containing pure liquid hydrogen, and immersed in the vacuum vessel surrounding the thermometer bulb to the depth of the top and the bottom of the latter respectively. The two sets of readings, of which the mean is given above, did not differ by more than 1 millim., indicating that the temperature of the thermometer bulb was uniform.

The following table shows the order of the agreement between the measurements of temperatures near the boiling-point.

### Hydrogen Scale.

Thermometer.	Observed vapour pressures.	Observed temperature.	Temperature from smoothed curves.
A	millims. 757·2	° 20·17	° 20·21
B	766·6	20·28	20·25

### Helium Scale.

Thermometer.	Observed vapour pressures.	Observed temperature.	Temperature from smoothed curves.
A	millims. 765·0	° 20·42	° 20·44
B	759·2	20·41	20·41
C	770·0	20·43	20·45
D	749·0	20·36	20·36

With regard to the measurements at lower pressures, the greatest difference between the observed and calculated temperatures in the first series of measurements with the helium thermometer exceeds 0·1. These errors can be accounted for by supposing that when the liquid hydrogen surrounding the thermometer bulb was made to boil under reduced pressure, the observations were made before the temperature of the thermometer bulb, and of the bulb containing the pure liquefied hydrogen, had become steady.

At pressures below 200 millims. it appeared to be much more easy to maintain a steady temperature than at intermediate pressures. In the last series of measurements, as has already been stated, two bulbs containing pure liquid hydrogen and connected with two manometers, were immersed at different levels in the vacuum vessel containing the liquid hydrogen surrounding the thermometer bulb, to the depth of the top and of the bottom of the thermometer bulb respectively. The pressures indicated by the manometers were read simultaneously and were never found to differ by more than 1 millim., proving that the temperature of the thermometer bulb was practically uniform.

In concluding these remarks on the accuracy of the results, it may be well to point out that the expression of differences of temperatures in degrees, particularly at low temperatures, in degrees, is somewhat apt to lead to a false conclusion. In dealing with the thermodynamic cycle, on which our idea of an absolute scale of temperature is

based, differences of temperature can only be expressed as fractions of the absolute temperature at which the processes in the cycle are performed. The accuracy of a thermometric measurement should then be as expressed not as  $\Delta T$  but as  $\Delta T/T$ ; this leads us to the conclusion that an error of  $0^{\circ}01$  at the boiling-point of hydrogen is equivalent to an error of  $0^{\circ}15$  at the normal temperature.

9. *The Vapour Pressures of Liquid Hydrogen.*

Pressures in millimetres of mercury.	Temperatures on the hydrogen scale.	Temperatures on the helium scale.
800	20°41	20°60
790	20·36	20·55
780	20·32	20·51
770	20·27	20·46
760	20·22	20·41
750	20·17	20·36
740	20·13	20·31
730	20·08	20·26
720	20·03	20·21
710	19·98	20·16
700	19·93	20·12
650	19·68	19·87
600	19·41	19·61
550	19·13	19·33
500	18·82	19·03
450	18·50	18·70
400	18·15	18·35
350	17·78	17·98
300	17·36	17·57
250	16·90	17·11
200	16·37	16·58
150	15·74	15·95
100	14·93	15·14
50	—	14·11

10. *Discussions of the Results.*

As has already been pointed out in Part II. of this research, the temperatures measured on the scale of the two thermometers differ by  $0\cdot1$  at the temperature of liquid oxygen. It is not, therefore, surprising to find that at the temperatures of liquid hydrogen the two scales differ to an even greater extent. A glance at the vapour-pressure curves of liquid hydrogen on the helium and hydrogen scales will show that the temperatures on the helium scale lie almost exactly  $0\cdot20$  above those on the hydrogen scale. Such a difference was, as we have already pointed out, to be expected (Part II., p. 152), but in the present state of our knowledge of the properties of these gases at low temperatures further discussion of these results is impossible.

APPENDIX I.—*On the Melting-Point of Hydrogen.*

DEWAR ('Roy. Soc. Proc.,' 1891, vol. 68, p. 360) states that the melting-point of hydrogen on the helium scale is  $16^{\circ}$ . The method by which the measurement was made has not been recorded; he had previously given the melting pressure as 55 millims. (see p. 106). Our experiments of the vapour pressures of hydrogen appeared to indicate that the melting-point lay considerably below the temperature given by DEWAR, for not only did the numerical results bear evidence that at temperatures close to  $14^{\circ}$  we were still dealing with liquid, but when after maintaining a pressure of 55 millims. in the apparatus for some time the vacuum vessel was found to contain liquid only. We therefore decided to carry out a separate experiment with a view to determining the exact melting-point.

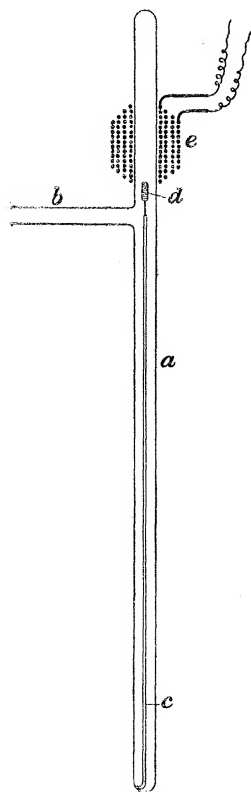


Fig. 2.

The apparatus employed in this experiment is shown in fig. 2. The tube *a*, which was 6 millims. in diameter, and 150 millims. long below the side tube *b*, passed through the rubber stopper *p* of the apparatus shown in fig. 1, so that the lower end of it lay at the level of the middle of the thermometer bulb. The tube *a* contained a very thin glass rod, *c*, bent at its lower end into a hook, and joined at the top to a piece of soft iron wire wound into a solid spiral, *d*. Round the tube *a* above the side tube a coil of insulated wire was wound forming a solenoid; by passing a current through the coil, the rod *c* with its iron head *d* could be given a vertical motion of about 3 millims.

The side tube *b* communicated with a mercury reservoir containing pure hydrogen from palladium, with a manometer of the type described in Part II. (fig. 2), and through a stop-cock with the mercury pump.

In carrying out the experiment the lower part of the tube *a* and the thermometer bulb were cooled in liquid hydrogen boiling under reduced pressure in the manner described on p. 160, and about 100 cub. centims. of gaseous hydrogen was allowed to enter and liquefy in it. At all temperatures down to  $14^{\circ}2$ , which corresponded to the lowest pressure which we were able to obtain under the conditions of the experiment, the hydrogen appeared to remain liquid, for, on passing the current through the solenoid, the piece of iron *d* was seen to move upwards.

Maintaining the temperature outside *a* at from  $14^{\circ}2$  to  $14^{\circ}8$ , the stop-cock connecting the side tube *b* with the mercury pump was opened for a moment. The pressure in the apparatus immediately fell to 49 millims., and remained steady there

while the stop-cock was open; on passing the current through the solenoid the piece of iron *d* did not move, indicating that its lower end was embedded in solid hydrogen. The stop-cock leading to the pump was then closed, and when the hydrogen in the tube *a* had melted it was again opened and the melting pressure was again determined. This operation was repeated several times; the melting pressure was invariably found to be 49 or 50 millims. This pressure corresponds to a temperature of  $14^{\circ}\cdot 1$  on the helium scale, which is the melting-point of hydrogen.

APPENDIX II.—*Note on the Preparation of Pure Hydrogen.*

It is obvious that the simplest method for the preparation of pure dry hydrogen would be to liquefy some of the gas in a bulb immersed in liquid hydrogen and allow the gas to evaporate directly into the apparatus which it is intended to fill. At the temperature of liquid hydrogen all possible impurities would be practically non-volatile, and the gas would not require further purification.

The hydrogen employed in these researches was obtained by the action of dilute sulphuric acid on pure platinised zinc. The gas was passed through a solution of potassium permanganate, and through a tube containing pentoxide of phosphorus into a tube fitted with a stop-cock containing pieces of palladium sponge. When the palladium was saturated, the stop-cock was closed and the tube connected with it was sealed to the apparatus for filling the thermometer. The gas from the palladium tube passed through a tube, about 40 centims. long, containing pentoxide of phosphorus, through a large bulb filled with glass beads and immersed in liquid air, to the inlet tube of the thermometer. The apparatus also communicated through a stop-cock with the mercury pump and with a mercury manometer. Before filling the thermometer the whole apparatus was exhausted and a considerable quantity of hydrogen allowed to escape from the palladium. The actual operations involved in filling the thermometer have already been described (p. 117); it is only necessary to state here that every precaution was taken to avoid contamination of the gas by moisture or by other impurities.

APPENDIX III.—*Note on the Preparation of Pure Helium.*

As has been pointed out by one of us (TRAVERS, 'The Experimental Study of Gases'), the constant-volume helium thermometer furnishes the only reliable means of measuring low temperatures. For the purpose of measuring the temperature of liquid hydrogen boiling under reduced pressure, it is of particular importance that the helium should be free not only from argon, but even from neon; for as that element has a vapour pressure of 12·8 millims. of mercury at the boiling-point of liquid hydrogen, and 2·4 millims. at  $15^{\circ}\cdot 65$  abs., its vapour pressure at  $14^{\circ}$  abs. would

probably be less than 1 millim. of mercury, and consequently a very small quantity of this impurity would be sufficient to vitiate the results.

As it is obviously impossible to separate neon completely from helium by cooling the gas to the temperature of liquid hydrogen, it is necessary to employ helium which is initially as free from that gas as is possible. DEWAR (*loc. cit.*, p. 155) has employed the gas from the Bath springs as a source of helium, but, as his own investigations show that the resulting helium contains 7.4 per cent. of neon, it is unsuitable for thermometric purposes, particularly for the measurement of the temperature, which can be obtained by boiling hydrogen under reduced pressure.

Some years ago it was shown (RAMSAY and TRAVERS, 'Roy. Soc. Proc.' vol. 60, p. 206) that by subjecting the gas from the mineral clèveite to the process of fractional diffusion, it was possible to separate from it a small quantity of argon and to reduce the density of the lighter fraction to 1.98 ( $O = 16$ ). Later it was found by one of us, though the experiment has not been recorded, that when the gas from clèveite was passed through liquid oxygen, cooled to  $-210^{\circ}\text{C}$ . in a bulb immersed in liquid air boiling under reduced pressure, a small quantity of argon was removed from the gas, but apparently no neon. For this reason clèveite gas appeared to be the most suitable source for obtaining pure helium. The light helium obtained by the diffusion experiments was employed in these researches; it was purified by passing it at the normal pressure through a coil immersed in liquid hydrogen.

The apparatus employed will now be described.

The gas, of which we had about 180 cub. centims., was introduced through the syphon (fig. 3), into the gas-holder A, which contained mercury. The gas-holder was connected by a rubber tube with a mercury reservoir not shown in the figure, and in order to eliminate any risk of air entering the gas-holder through leakage of the rubber tube, the connection was made through a trap, D. The gas-holder communicated through the two-way stop-cock, B, with the syphon for introducing the gas, and with the refrigerating coil C, which led through a second stop-cock, B, to a second gas-holder similar to the first. The coil communicated with the mercury pump through the stop-cock E.

After thoroughly exhausting the coil, the stop-cock E was closed, and the gas admitted to it. A vacuum vessel containing about 300 cub. centims. of liquid hydrogen, surrounded by a larger vessel containing liquid air, was brought below the coil and raised till the latter was thoroughly immersed in the liquid. The stop-cocks B, and B, were then carefully opened, and by adjusting the level of the mercury reservoir connected with the gas-holders, the gas was passed three times backward and forward through the coil. When the whole of the gas had returned to the first gas-holder, the stop-cocks were closed. The gas in the gas-holder we called fraction 1.

About 100 cub. centims. of the original gas, measured under normal conditions, still remained in the coil, for at the boiling-point of liquid hydrogen a gas occupies only about 1/15 of the volume which it fills at the normal temperature. On opening the



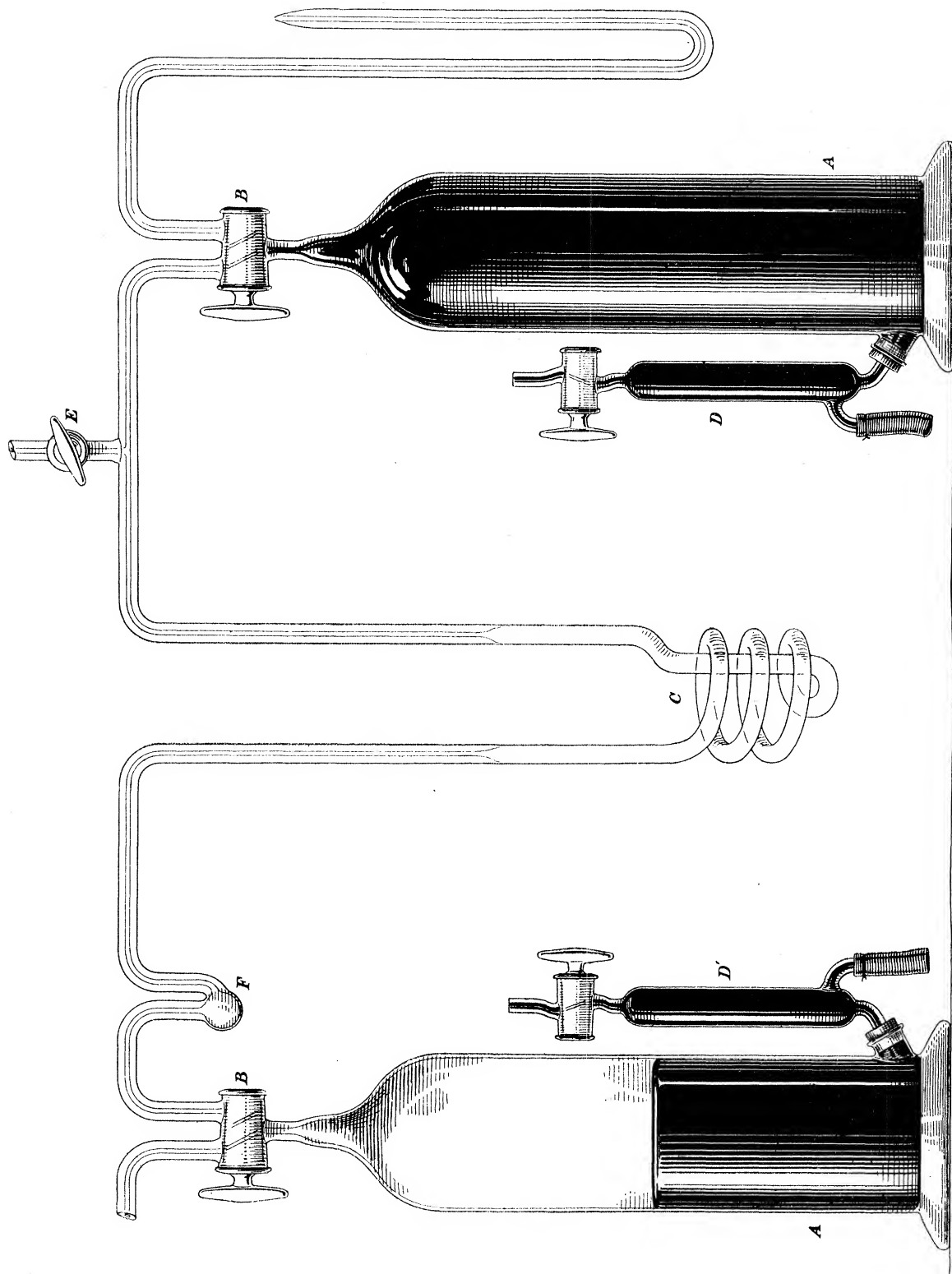


Fig. 3.

stop-cock E for a moment, about 70 cub. centims. of the gas passed into the pump. This fraction (2) was probably as pure as fraction 1, for the additional cooling produced by its sudden expansion would compensate for the tendency of any light impurity to evaporate; it was, however, kept separate (fraction 2).

When fraction 2 had been pumped off and collected, the stop-cock E was again opened, and the remaining volatile gas was pumped off and collected. It formed fraction 3, and consisted of about 25 cub. centims. of gas. Finally the liquid hydrogen was removed, and the residue in the coil, which volatilised and passed into the pump, was collected as fraction 4.

Fraction 4 was found to consist largely of nitrogen, which had probably entered the tube in which the gas had been stored since 1898 at the time it was last handled. This gas was sparked with oxygen over potash for some hours, and after removal of the excess of oxygen about 0.5 cub. centim. of gas was left; it was found on spectroscopic examination to consist of argon and krypton only, showing the spectrum of the latter with brilliancy.

The fact that clèveite helium yields krypton indicates that that gas must be present in the original mineral. As krypton is present in air to an extent not greater than 1 part in 1,000,000, the presence of that gas in the helium could not possibly be due to leakage of air into the apparatus. The quantity of krypton, like mercury vapour, which is necessary to give a brilliant spectrum in presence of argon, is exceedingly small, and possibly the total quantity of krypton in the gas might not exceed 0.01 cub. centim., or 0.005 per cent. on the original helium. It is interesting to note that when OLSZEWSKI attempted to liquefy helium by compressing it at  $-210^{\circ}\text{C}.$ , and allowing it to expand ('Nature' 1896, vol. 62, p. 244), a small quantity of a white substance separated. It is intended on another occasion to investigate the heavy fraction of gas obtained in 1898 by the diffusion of helium.

The first fraction of gas, which we called fraction 1, was used in the first series of measurements of the boiling-point and vapour pressures of liquid hydrogen down to  $15.5^{\circ}\text{abs.}$  Fractions 1 and 2 were subsequently mixed and passed a second time through a coil immersed in liquid hydrogen directly into the large constant-volume thermometer for the measurement of the pressure coefficient (p. 129), which was found to be 0.00366255.

For the second series of measurements of the vapour pressures of liquid hydrogen the helium was further purified by passing it through a coil immersed in liquid hydrogen boiling under reduced pressure. For this purpose the coil c, through which the helium was passed (fig. 3), was enclosed within an apparatus similar to that employed in determining the vapour pressure of hydrogen. The arrangement which is shown in fig. 4 requires little description. The vacuum vessel containing the liquid hydrogen was introduced from below into the wide (p. 160) tube so as to surround the coil and the bulb which contained the pure hydrogen, and was connected with a manometer by which the vapour pressure on the pure hydrogen, and from this

the temperature of the coil could be determined. By means of the exhaust pump the temperature of the liquid hydrogen was reduced to 110 millims. of mercury, corresponding to a temperature of  $15^{\circ}3$  abs. Helium was then allowed to fill the coil at normal pressure, and by opening the stop-cock the gas was slowly admitted into the thermometers, which had previously been exhausted.\*

APPENDIX IV.—*Note on the Vapour Pressures of Solid Neon.*

The following experiments are of interest both with regard to their application to the preparation of pure helium and to the light they throw on the homogeneity of neon.

In the first experiment the neon was condensed in a fractionating bulb (RAMSAY and TRAVERS, 'Phil. Trans.' 1901, vol. 197, A, p. 51) which was connected with a manometer reading pressures below 100 millims. of mercury and, through a stop-cock, with a mercury pump. About 20 cub. centims. of neon were introduced into the bulb and condensed by cooling it by means of liquid hydrogen, boiling under the normal pressure ( $20^{\circ}4$  on the helium scale). The vapour pressure observed by means of the manometer was 12.8 millims. of mercury. On opening the stop-cock, and allowing some of the neon to evaporate into the pump, the pressure fell momentarily, but on closing it the pressure again rose to 12.8 millims. The operation was repeated several times with the same result, proving that neon is a homogeneous substance. On removing the vacuum vessel containing the liquid hydrogen, a small quantity of solid neon was seen in the fractionating bulb.

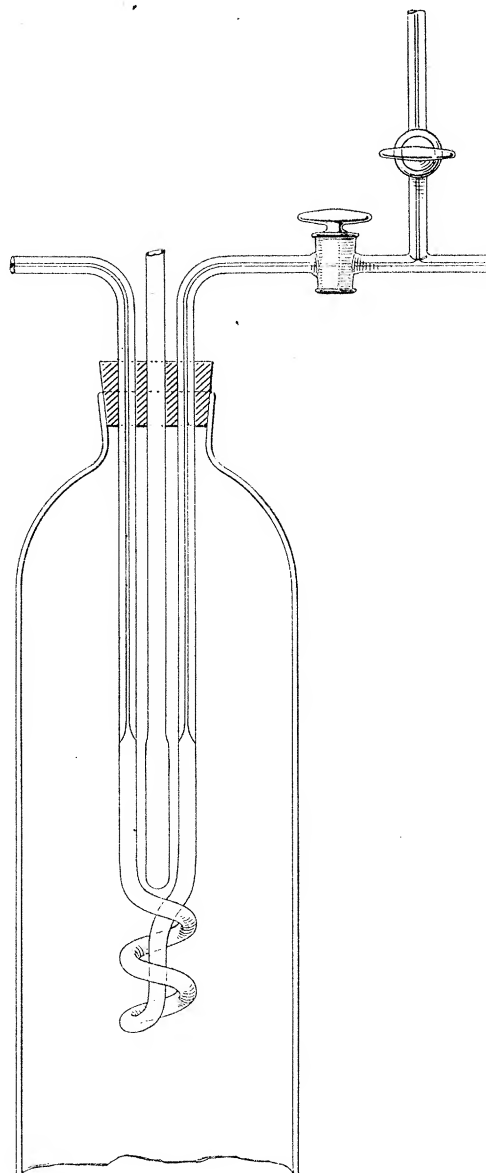


Fig. 4.

\* NOTE, *July 19th*, 1902. —After filling the thermometer, the greater portion of the gas contained in the coil, which was maintained at  $15^{\circ}3$  abs., was allowed to escape into the mercury pump, by opening the stop-cock communicating with it for a few seconds. When this gas had been pumped off, the stop-cock was again opened, and the remaining gas was collected separately. The last fraction, which consisted of about 10 cub. centims., was examined spectroscopically, but it appeared to contain no trace of neon.

In the second experiment, the neon was introduced into the bulb *m* of the apparatus employed in determining the vapour pressure of liquid hydrogen (fig. 1). At a temperature of 15°·65 (helium scale), the vapour pressure of the neon was 2·4 millims. of mercury.

APPENDIX V.—*On the Probable Values of the Critical and Boiling-Points of Helium, and on an Attempt to Liquefy that Gas.*

As the foregoing results show, helium behaves at low temperature as a more perfect gas than hydrogen, and even if no further data were forthcoming, one would expect to find that its critical and boiling-points were lower than those of the latter gas. This, as we shall presently show, receives further confirmation from theoretical considerations and from experimental results.

In 1892, OLSZEWSKI (*loc. cit.*, p. 174) showed that when helium, under a pressure of 80 atmospheres, was cooled to  $-210^{\circ}\text{C}$ ., and suddenly allowed to expand till the pressure fell to that of the atmosphere, no mist was seen in the compression tube. More recently ('Roy. Soc. Proc.', 1901, vol. 68, p. 360) DEWAR performed a similar experiment, cooling the compression tube in hydrogen reduced to its freezing-point. He did not, however, succeed in liquefying the gas, which he believed to have been cooled to  $9^{\circ}$  or  $10^{\circ}$  absolute, the temperature which he assigns to the upper limiting value of its critical point.

Though by compressing any gas, and subsequently allowing it to expand adiabatically, the relationship between the initial and final pressures  $p$ ,  $p'$  and the initial and final temperatures  $T$ ,  $T'$  can be found by the equation

$$\frac{T}{T'} = \left(\frac{p}{p'}\right)^{\frac{k-1}{k}},$$

when  $k$  is the ratio of the specific heats for the gas, this equation may not be applicable to the case in which a gas is compressed into a capillary tube and then allowed to expand, the thermal capacity of the gas being then very small compared with that of the walls of the containing tube.

It occurred to us that if we could cool a few centimetres of a compression-tube containing helium down to a temperature below the critical point of the gas, then, on compressing the gas, its volume would decrease and the pressure would rise till the vapour pressure of helium corresponding to that particular temperature was reached. It should then be possible, supposing the gas to be homogeneous, to decrease the volume of the helium without increasing the pressure, as a change in the volume of the gas would imply liquefaction in the cooled portion of the tube. Before describing our experiments we will first deal with the probable value of the critical and boiling-points of helium.

Of the five gases, helium, neon, argon, krypton, and xenon, the vapour pressures and critical constants of the last three only have been determined. They are as follows (RAMSAY and TRAVERS, 'Phil. Trans.,' A, 1901, vol. 197, p. 47).

	Atomic weight.	Boiling-point.	Critical point.	Ratio.
Helium . . . .	4	—	—	—
Neon . . . .	20	—	—	—
Argon . . . .	40	87 abs.	155 abs.	0·561
Krypton . . . .	82·5	121 „	210 „	0·576
Xenon . . . .	128	164 „	288 „	0·568

It will be observed that the ratios of the absolute boiling-points to the absolute critical points has a nearly constant value, the mean of the actual ratios being 0·57. This relationship is common among similar substances, for which the boiling and critical temperatures may be considered as corresponding states.

The boiling and critical points of neon are not known. We are certain, however, that the critical point lies below 60° abs., and, as the vapour pressure is 12·8 millims. at 20°·4 abs. the boiling-point must lie above 25° abs. If the ratio for the critical and boiling-points is the same as for the other gases, viz., 0·57, we may calculate the temperature of the boiling and critical points which will correspond.

Boiling-point . . .	28°·5	. . .	31°	. . .	34°.
Critical point . . .	50°	. . .	55°	. . .	60°.

In the paper in the 'Philosophical Transactions' already referred to, it was pointed out that argon, krypton, and xenon resemble one another, though krypton bears a stronger resemblance to neon and helium, forming, in fact, a link between the two sub-series of this group of elements. If now we plot (fig. 5) on a diagram the critical and boiling-points of the elements as ordinates and their atomic weights as abscissæ, the points representing argon, krypton, and xenon lie on a straight line. Taking 30 abs. as the boiling-point and 53 abs. as the critical point of neon, and plotting these points on the diagram against the atomic weight of neon, we find that the lines joining these points to the corresponding points for krypton, when prolonged, pass through the origin of the axes. If the points corresponding to helium lie also on these lines, the critical and boiling-points of this gas will be 10° and 6° abs. Even if we assign to the critical point of neon its upper limiting value 60° abs., and suppose the points on the diagram representing krypton, neon, and helium to lie on a curve, the critical point of helium cannot be far above 12° abs.

In our experiments the helium was compressed in the compression tube of an apparatus similar to that employed by CAILLETET or AMAGAT, only the pressure was transmitted to the surface of the mercury by means of compressed air, instead of

employing liquid and a pump. The compression tube is shown in fig. 6. The wider portion, A, which was made of boiler-gauge tube, had an internal diameter

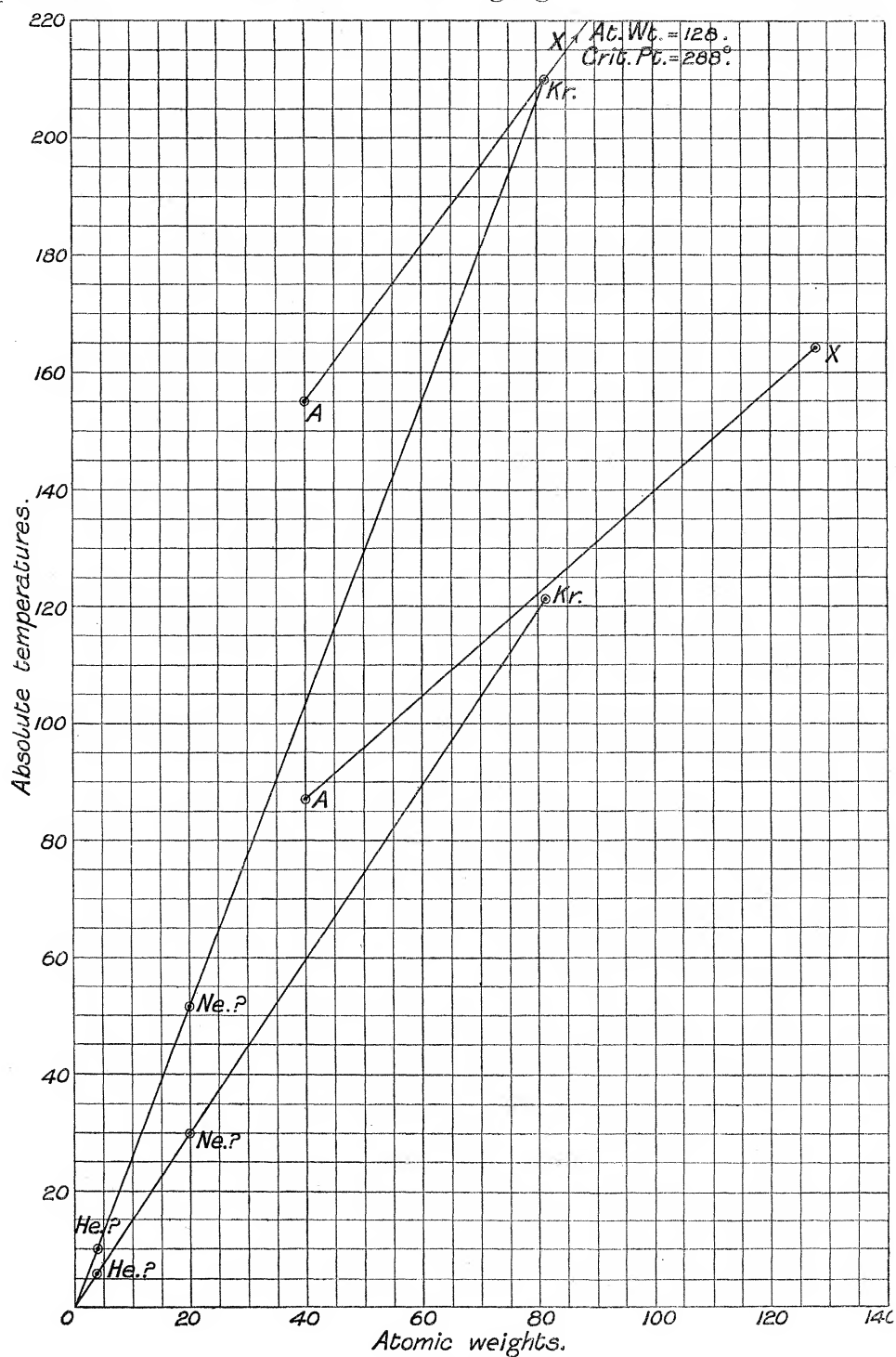


Fig. 5.

of 6 millims., and was capable of standing a pressure of 80 atmospheres, or more. At its lower end it entered the steel compression apparatus, and at the top it was

sealed to the capillary tube B, which had an internal diameter of 0.5 millim. When the lower portion of the tube B was cooled to the lowest temperature, it required a pressure of 60 atmospheres to compress the whole of the helium into the capillary tube.

The pressure on the helium was determined by means of two gauges of the Amagat type, filled with nitrogen, and indicating pressures from 2 to 12 atmospheres, and from 8 to 60 atmospheres respectively.

The compression tube was filled with pure helium prepared in the manner described on p. 174 (fraction 1).

In our first experiment the capillary compression tube was enclosed together with the thermometer bulb, &c., in the apparatus shown in fig. 1 (see also p. 160). At temperatures between  $20^{\circ}5$  and  $14^{\circ}$  abs. (helium scale), the pressure on the gas was slowly increased to 60 atmospheres, and then slowly reduced. Under all conditions the smallest change in the position of the mercury meniscus in the compression tube was always accompanied by a corresponding change in the pressure. This experiment was repeated on three occasions.

In another set of experiments, the capillary portion B of the compression tube passed through a rubber stopper E (fig. 6) into a small silvered vacuum vessel C, with a contracted mouth, enclosed within a wider glass tube D, sealed at the bottom to a tube G, 7 millims. in diameter, and fitting closely to the rubber stopper E. The upper part of the tube D contained a plug of natural wool wrapped in gauze, to shield the mouth of the vacuum vessel from radiation from above. A tube F passed through the stopper E, and was connected with a mercury manometer which served to measure the pressure in D.

The vacuum vessel C was filled with liquid hydrogen and placed in the tube D, which was then rapidly fitted to the rubber stopper E; the compression tube B had previously been cooled with liquid air. A vacuum vessel H containing liquid air was then brought outside the tube D as in fig. 6. The tube G was connected with the double 'Fleuss' pump, arranged with the cylinders in series (p. 161), and the pressure on the liquid hydrogen was reduced to 5 millims. of mercury, and maintained at that pressure for 20 minutes. Even at this temperature, which is probably not far below  $13^{\circ}$  abs., no evidence could be obtained that helium had liquefied.

The extremely permanent character of helium confirms our view that that gas is by

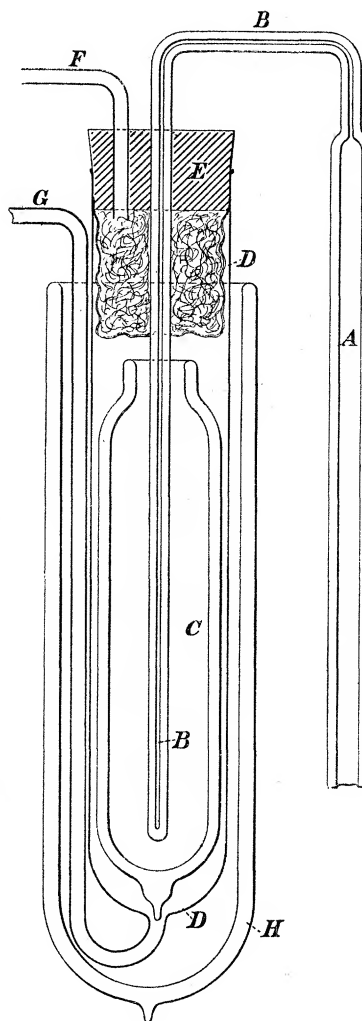


Fig. 6.

far the most perfect thermometric substance known to us. Possibly, even at the lowest temperature that we have arrived at, the temperatures measured on the constant-volume helium scale are not far from absolute measurements.

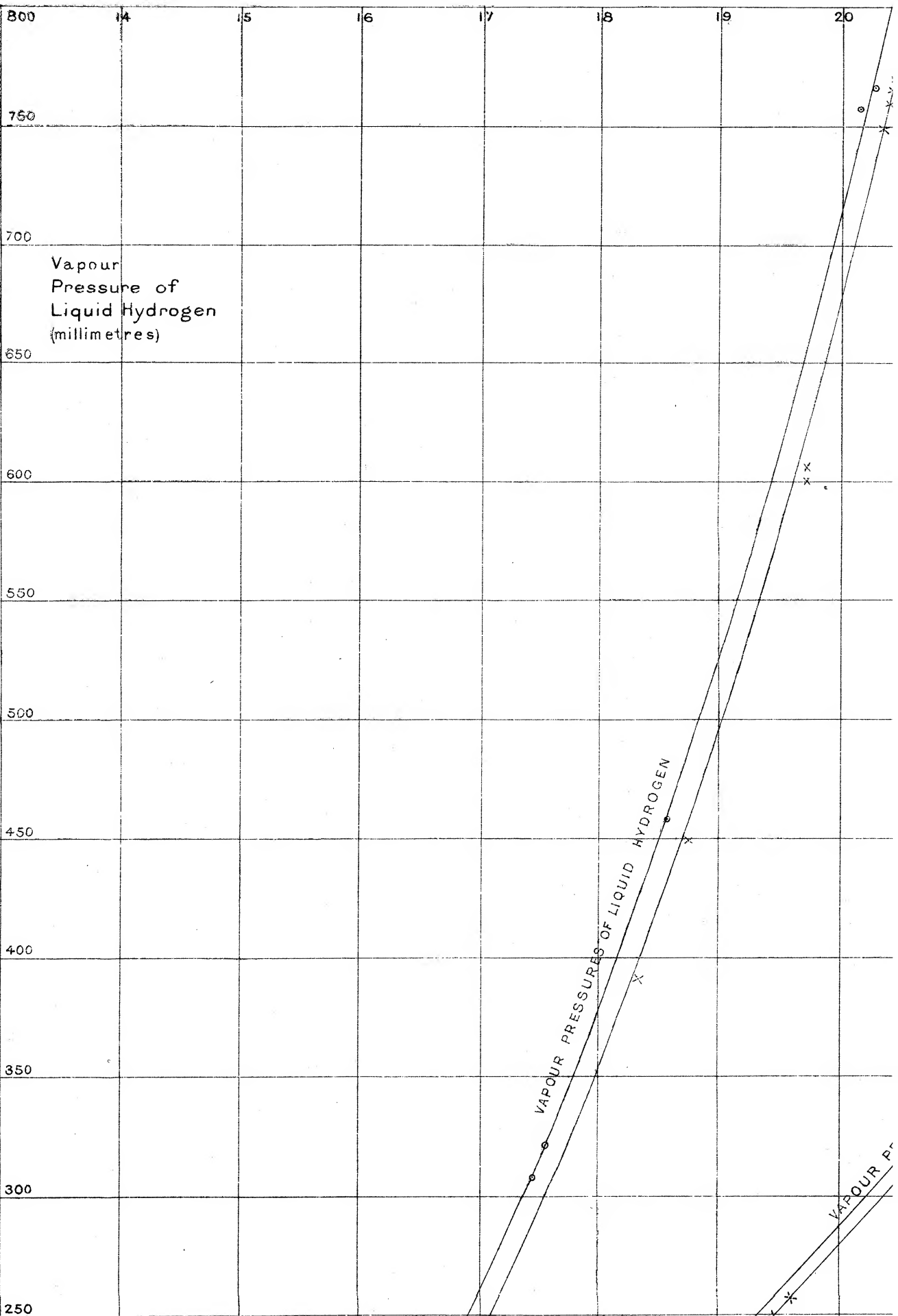
Turning to the question of liquefying helium, it would of course be possible to compress large quantities of the gas, and allowing it to expand adiabatically to at least produce a mist of helium. As the compression could only be effected in vessels with walls of considerable thickness, it would probably be impossible to produce any quantity of liquid in this way. With regard to the application of the regenerative process, which can so easily be employed in the case of air or of hydrogen, to the liquefaction of helium, we can say nothing; for apart from the experimental difficulties involved in the problem, we do not yet know whether helium becomes heated or cooled when allowed to expand freely at high or at low temperatures.

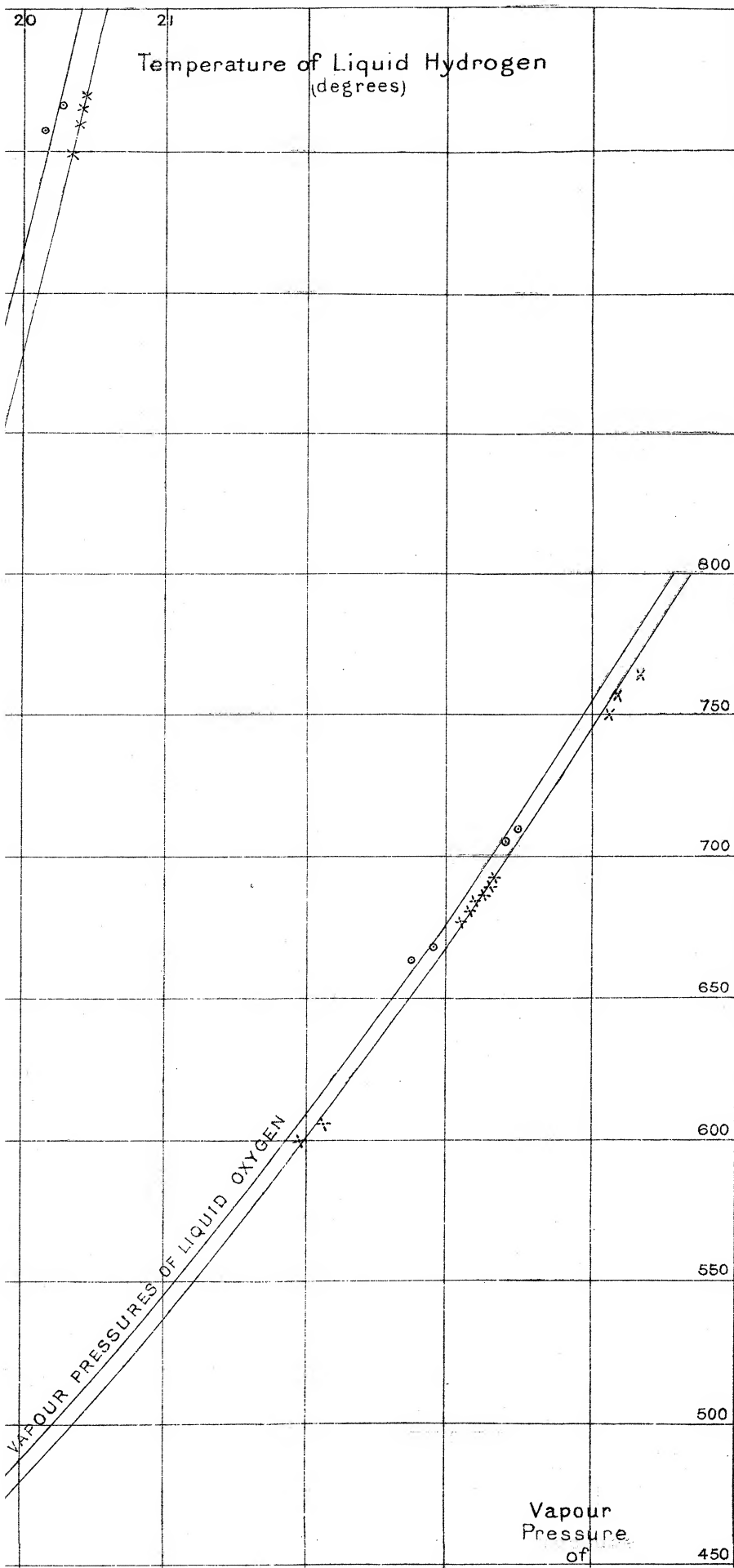
From this point of view, and for the correction of gas thermometers, the Joule-Thomson effect for helium should be determined over a wide range of temperature.

In conclusion, we wish to express our thanks to the Government-Grant Committee of the Royal Society for the assistance they have given us in carrying out this investigation.

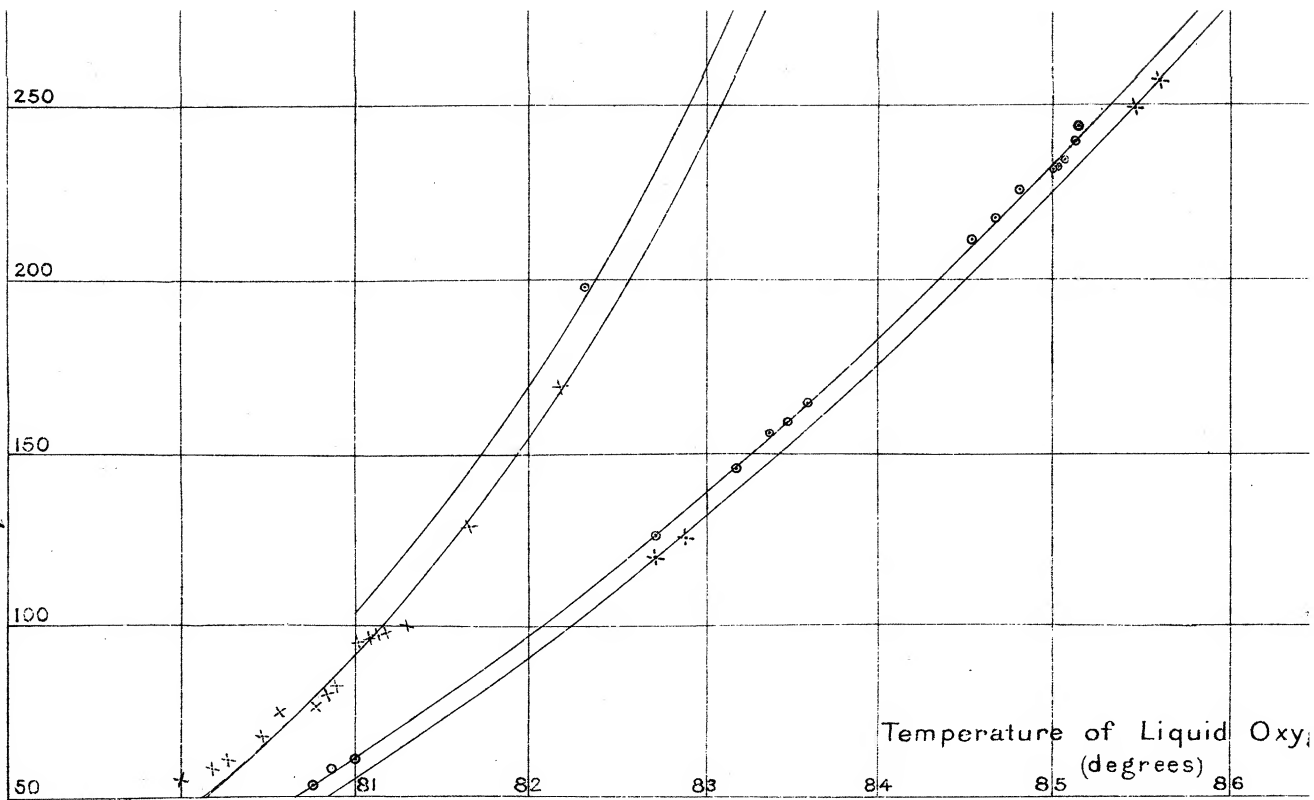
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Huth, Litt' London



Vapour Pressure of Liquid Oxygen (millimetres)

Temperature (°C)	Vapour Pressure (mmHg)
-183	250
-180	350 (Point X)
-118	450

On Hydrogen Scale  
On Helium Scale

